U.S. DEPARTMENT OF COMMERCE
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PB-257 688

Development of Selective Hydrocarbon Sampling System and Field Evaluation with Conventional Analytical System

Analytical Research Labs., Inc.

Prepared for

National Environmental Research Center, Research Triangle Park, N C

Aug 75

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-650/2-75-050	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: Development of Selective Hydrocarbon Sampling System and Field Evaluation with Conventional Analytical System	5. REPORT DATE: August 1975
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Dr. Arthur F. Isbell, Jr.	8. PERFORMING ORGANIZATION REPORT NO. 2501-F
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Analytical Research Laboratories, Inc. 160 Taylor Street Monrovia, California 91016	10. PROGRAM ELEMENT NO. 1AA010
	11. CONTRACT/GRANT NO. 68-02-1201
12. SPONSORING AGENCY NAME AND ADDRESS: U.S. Environmental Protection Agency Chemistry and Physics Laboratory National Environmental Research Center Research Triangle Park, N.C. 27711	13. TYPE OF REPORT AND PERIOD COVERED: Final Report
	14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A sampling system was designed to permit the determination of the saturate, unsaturate, aromatic, and oxycarbon content of stationary-source hydrocarbon vapor emissions. A Joy Manufacturing Company Method 5 stack sampler was modified to incorporate a vapor collector cartridge that quantitatively traps all volatile hydrocarbons present in the sampled gas stream. The Class Analyzer desorbs the sample from this Universal Collector and passes it through a system of class abstractors that remove certain hydrocarbon classes while permitting the remainder of the sample to pass into cryogenic traps. The contents of each trap are desorbed sequentially through an external flame ionization detector. The quantity of each class present in the sample is calculated from the detector responses to the effluents from the various class abstractor streams.

Detailed evaluations of the Universal Collector and class abstractor candidates are presented. Test results of the complete sampling and analytical system are included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Gas sampling, flue gases, concentrating, sorption, chromatographic analysis, alkanes, unsaturated hydrocarbons, aromatic hydrocarbons, alcohols, aldehydes, ketones.	Selective hydrocarbon sampling system, hydrocarbon class analyzer	07/03, 07/04, 14/02

18. DISTRIBUTION STATEMENT: Unrestricted	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 69
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: $4.50/2.25

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

271055

PB 257 688

EPA-650/2-75-050

August 1975

Environmental Protection Agency Technology Series

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INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-650/2-75-050

DEVELOPMENT OF SELECTIVE HYDROCARBON SAMPLING SYSTEM AND FIELD EVALUATION WITH CONVENTIONAL ANALYTICAL SYSTEM

by

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Contract No. 68-02-1201
ROAP No. 26AAP-30
Program Element No. 1AA010

EPA Project Officer: James B. Homolya

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON, D.C. 20460

August 1975

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Publication No. EPA-650/2-75-050

ABSTRACT

A sampling and analytical system was designed to permit the routine determination of the saturate, unsaturate, aromatic, and oxycarbon content of stationary-source hydrocarbon vapor emissions. The intent has been to lend great definition to the traditional total hydrocarbon analysis.

A Joy Manufacturing Company Method 5 stack sampler has been modified to incorporate a vapor collector cartridge which quantitatively traps all volatile hydrocarbons present in the sampled gas stream.

The Class Analyzer desorbs the sample from this Universal Collector and passes it through a system of class abstractors which remove certain hydrocarbon classes while permitting the remainder of the sample to pass into cryogenic traps.

The contents of each trap are desorbed sequentially through an external hydrocarbon (flame ionization) detector. The quantity of each class present in the sample can be calculated from the detector responses to the effluents from the various class abstractor streams.

Detailed evaluations of the Universal Collector and class abstractor candidates are presented. Test results of the complete sampling and analytical system are included.

The stack sampler and Class Analyzer serve as models for instrumentation which will permit technicians to sample and analyze stationary source emissions by hydrocarbon class.

This report was submitted in fulfillment of Contract Number 68-02-1201 by the Analytical Research Laboratories, Inc., under the sponsorship of the Environmental Protection Agency. Work was completed as of December 1974.

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SECTION I

CONCLUSIONS

The combined collection, class-separation, and individual determination of the saturate, unsaturate, aromatic, and oxycarbon fractions of volatile hydrocarbons in stationary source emissions is feasible. The principle employed in the Class Analyzer, however, will have to be further explored and developed before it can be made applicable for the selective determination of halocarbons.

The operation of the Class Analyzer directly on stream is not practical. The volatile hydrocarbons must first be accumulated on an adsorbent and then desorbed into the Class Analyzer. The "Universal Collector" developed on this program successfully fulfills this requirement.

Simultaneous volatile hydrocarbon sampling (with the Universal Collector) and particulate collection can be achieved using a modified EPA Reference Method 5 stack sampler. Sample streams having high moisture levels are troublesome. Decoupling the Universal Collector from the stack sampler for interfacing with the Class Analyzer is reasonably facile.

The use of a field-practical detector in the modified stack sampler to signal hydrocarbon breakthrough from the Universal Collector does not appear feasible. Careful adherence to proper sampling procedures should, however, obviate premature overloads of the Universal Collector.

Several design refinements of the bread-board Class Analyzer are necessary before it can be advanced to prototypic hardware quality. Contamination from the Universal Collector and the Class Analyzer comprise intrinsic problems requiring further attention.

Utilization of the very steps of the selective hydrocarbon sampling and analysis procedure will not require extensive training or qualifications on the part of the user. The results of the program

lead to the conclusion that routine sampling and analysis of stationary source emissions by technicians will be possible after minor refinements of the designs thus far developed have been effected.

SECTION II

RECOMMENDATIONS

The Class Analyzer design should be modified to incorporate several needed changes. The plumbing layout can be improved and less retentive wall materials employed. The use of heated, teflon-lined tubing could be used to provide the latter enhancement. System flow rates downstream of the traps should be stabilized by incorporating suitable flow controllers. Any such devices used should not, however, contaminate or hold up the sample. Means should be provided for heating the trap more rapidly once the cryogenic baths are removed. An electrical configuration would probably be best suited for this purpose. A flame ionization detector (FID) with a signal-processing system should be made an integral part of the Class Analyzer. Also, it may be desirable to incorporate in tandem an electron capture detector for the purpose of estimating halocarbon contributions.

For optimum performance of the Class Analyzer, water vapor should be removed. A desiccant could be placed in the filter oven of the stack sampler upstream of the Universal Collector. Studies are needed, however, to establish the efficiencies of various desiccants and their inertness toward sample constituents.

Optimum preconditioning of the AC charcoal used in the Universal Collector must be established. Thermal conditioning at high temperatures causes partial sample loss while low temperature conditioning does not remove surface contaminants which continually bleed-off into the sample.

SECTION III

INTRODUCTION

The heavy contribution of hydrocarbon emissions (in the present context, hydrocarbon emissions includes all volatile organics) to air pollution has been recognized for some time. Abating the effects of these emissions must necessarily involve identifying specific pollutants with their sources. Even when the nature of the emissions of a given stack is known, and means of controlling them are applied, monitoring on a continuous or periodic basis is essential to assure proper functioning of the emission control devices. Laborious and complex laboratory identification and quantitation must be replaced in part by more rapid test methods in order to cope with demands put upon the monitoring organization.

Field monitoring now involves the use of the Total Hydrocarbon Analyzer (THA) or the collection of a total representative sample of the emissions followed by detailed laboratory analysis of the collected sample. The latter analysis generally relied upon gas chromatographic techniques for the separation of the various components of the sample with identification of the fractions by different instrumental methods, or by correlation with known retention data. Such techniques are not readily amenable to field use, and do not furnish rapid results. Detection by optical dispersion and absorption or by flame ionization techniques provide rapidly attainable results for total organic carbon content, but without identifying the nature of the organic compounds. Much improvement would be realized if pollutants could be sampled and analytically catalogued into classes of compounds, such as saturates, unsaturates, aromatics, oxycarbons, halocarbons, etc. If an abstraction device could be designed that is unique for a specific class of compounds while rejecting others, similar to many of the semiquantitative Kitagawa-tube test kits, then a total carbon determination of the rejected fraction would permit the calculation, by difference, of the total organic emission that

falls in the abstracted class. Since much of the effect of a specific pollutant is attributable to the functionality of the substance, classification by functional group should be adequate for rapid and reasonable assessment of the pollution potential, without resorting to identification of each individual member of the class.

The purpose of the present program has been to develop and field test a system that will collect, separate, and release for analysis atmospheric hydrocarbon pollutants as discrete molecular-type classes. The overall system, on being interfaced with conventional analytical devices (a gas chromatograph or a THA) would permit selective determinations of such hydrocarbon classes as: saturate, unsaturate, aromatic, halocarbon, and oxycarbon fractions. The system would be used for sampling over various time periods and environments, including hot stack gases, hydrocarbon pollutants associated with stationary emission sources.

A non-cryogenic, isokinetic sampler capable of collecting all hydrocarbon vapors without wall losses, preventing the breakthrough of light hydrocarbon components from the collector, and furnishing isolated collection of preformed particulates was developed from standard sampling hardware. A special separation system was also developed into which the volatile contents of the sampler can be transferred by thermal or other forms of desorption. By means of stream splitting and selective abstraction of hydrocarbon classes on different, selected sorbents, analytical measurements of the classes is achievable.

The initial phase of the program consisted of a comprehensive literature survey to determine the extant knowledge in the field of sorption chemistry. The results of this survey permitted the selection of the best candidates for a hydrocarbon sampling device, the Universal Collector, and for hydrocarbon class abstractors for the Class Analyzer.

Phase II involved laboratory screening of suitable Universal Collector candidates. Based on the results of these experiments, six identical Universal Collectors were constructed.

The third phase consisted of the modification of a commercially-available EPA Reference Method 5 stack particulate sampler. The incorporation of the Universal Collector into the Method 5 Sampler resulted in a stack sampler capable of collecting both particulates as well as volatile hydrocarbons from a stationary source.

Laboratory evaluation of suitable class abstractor candidates comprised the fourth phase. A detailed analysis of the sorption properties of the various sorbents permitted the selection of a series of class abstractors which, when properly arranged, provided a class analysis of a collected hydrocarbon sample.

Phase V included the incorporation of the class abstractors into an analytical instrument, the Class Analyzer. This device separates the collected sample into various fractions which, when passed through an external THA or FID provides quantitative information about the class composition of the sample.

In the final phase of the program, the total system was subjected to field testing. Hydrocarbon samples from actual and simulated stationary sources were collected, using the modified Method 5 stack sampler. These samples were then introduced into the Class Analyzer for the quantitative determination of hydrocarbon class composition.

SECTION IV

HARDWARE DESIGN AND CONSTRUCTION AND EXPERIMENTAL SYSTEM FABRICATION

UNIVERSAL COLLECTOR (UC)

The test apparatus shown schematically in Figure 1 was designed for a comprehensive evaluation of UC candidates. The breakthrough and desorption volumes of a variety of volatile hydrocarbon samples were determinable at temperatures ranging from 0° to 400°. Cryogenic trapping of the sample itself or of the effluent from the UC candidate permitted further gas chromatographic analysis for sample composition or contamination by the UC candidate.

Sample flow control and measurement were provided by Brooks Model 8744B NRS flow controllers and a Fischer and Porter Lab-Crest Model 10A1460NB22B rotameter with a 55 ml/min maximum flow rate for air. Temperature control and sample detection were provided by a Perkin-Elmer 880 gas chromatograph equipped with a dual FID system. The FID response was recorded by a Leeds and Northrup Speedomax G strip chart recorder capable of chart speeds varying from 0.635 to 30.48 cm/min (0.25 to 12 in/min).

The tubing was made of 304 stainless steel with Swagelok brass fittings. All valve bodies were either 316 stainless steel, brass, or plated brass. Buna-N O-rings were used in the backflush valve.

Hydrocarbon samples were either purchased from Matheson Company as analyzed standards or mixed and analyzed gas chromatographically by ARLI. ARLI-prepared samples were mixed using a stainless steel vacuum-pressure rack using standard vacuum rack techniques.

The UC candidates usually required preparation prior to testing. Exceptions were uncoated 80-100 mesh Porapak Q and 60-80 mesh Tenax GC. Porapak Q coated with 3% OV-1 (methyl silicone gum) was prepared by dissolving 0.06g of OV-1 in chloroform in a 100 ml round-bottom flask. Two grams of Porapak Q were added to this solution. The chloroform was removed using a rotary vacuum evaporator with the round-bottom flask submerged in warm water.

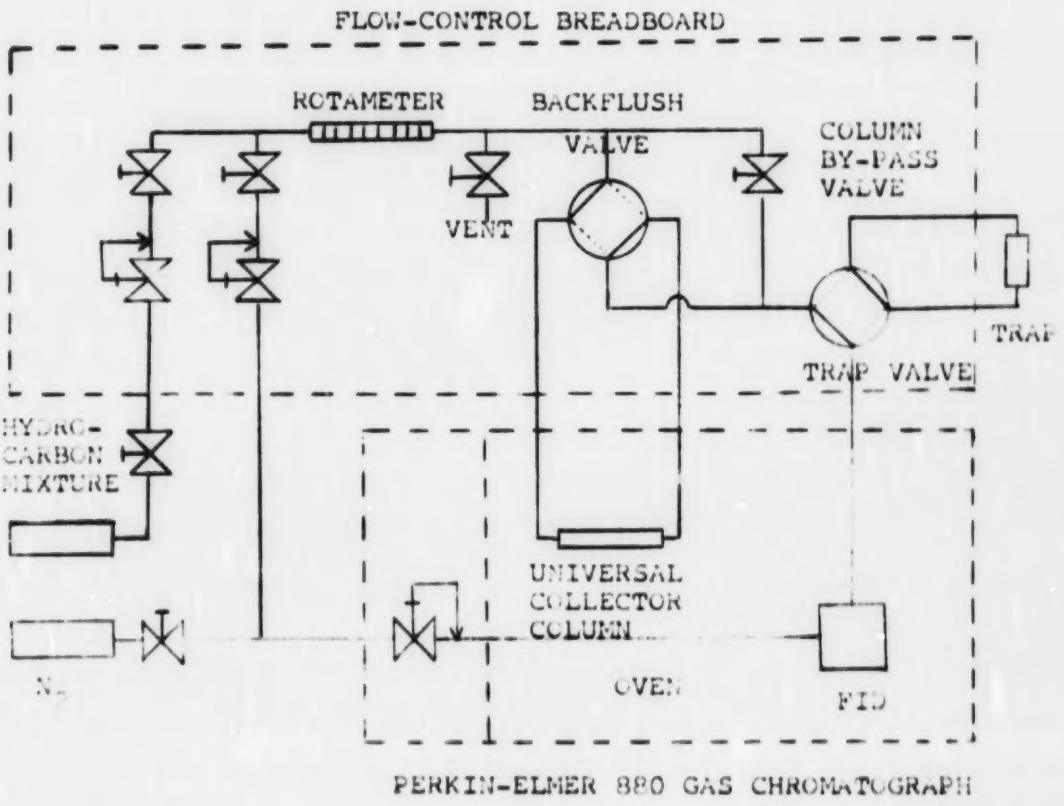


Figure 1. Schematic diagram of Universal Collector test apparatus

Most of the molecular sieve and charcoal candidates were manufactured in pellet form. These pellets were ground to either 60-80 or 80-100 mesh using a mortar and pestle.

For testing purposes, the UC candidates were packed in 20 by 0.64 cm O.D. stainless steel tubes. Each candidate was conditioned for about 2 hours at 200° under a 30 ml/min helium flow.

The final configuration of the UC is shown in Figure 2. Swagelok fittings are used throughout. Connecting fittings are 0.64 cm O.D. double-end shut-off quick-connect fittings. All fittings which might come into contact with corrosive substances are 316 stainless steel. The remaining fittings are brass or plated brass. All tubing is 304 stainless steel. The sorbent tubes measure 20 by 0.95 cm O.D. The remainder of the tubing is 0.64 cm O.D.

STACK SAMPLER

The original program plan called for the design and construction of a stack sampler. The Project Officer subsequently suggested that a more cost-effective approach would be to modify an off-the-shelf EPA Reference Method 5 particulate sampler.

Solicitations for Method 5 hardware were accordingly sent to a number of vendors. Bid specifications required the hardware to incorporate all necessary components to conform with EPA/APCO standards for Reference Method 5 as outlined in the Federal Register, Vol. 36, No. 247, except as noted below. The system should be encased, portable, operable on 115 VAC (60 Hz), and include (or exclude) the following options or dimensions:

- The sampling unit should include a filter assembly and cyclone. The filter assembly should be of the largest size normally provided by the vendor and should include three fritted glass discs and six gaskets. Filtering media should not be supplied.
- The sampling unit should not include the four liquid impingers and interconnecting hardware usually provided.

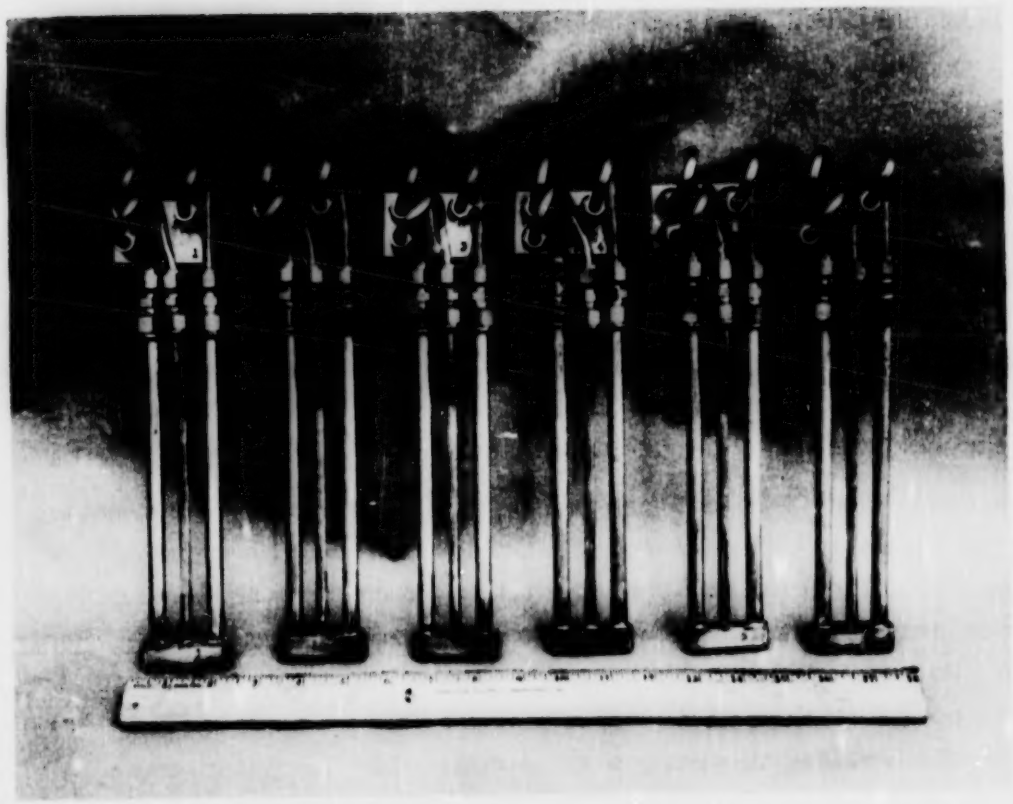


Figure 7. Universal Collectors

- The pitobe assembly should have an effective length of 1.5 m (5 ft). The internal surface of the sampling tube should be Pyrex glass or its equivalent. One each of three different sized sampling nozzles [0.64, 0.95, and 1.27 cm dia. (0.25, 0.375, and 0.50 in)] should be provided.
- Two nomographs should be supplied.
- The umbilical cord length should be 30.5 m (100 ft).
- The pitobe support system should be of a length appropriate to handle the specified pitobe.

After considering shipping costs, equipment specifications, some minor added requirements, and vendor location, a decision was made to purchase the Joy Method 5 stack sampler (Figure 3). Most of the other models considered would probably have served as well.

The Joy stack sampler is composed of two basic units: (1) the control unit, which contains the pump, heater controls, temperature gauge, and air flow measuring and control devices; and (2) the sampling unit, which contains the heated pitobe, the filter oven, and the impinger train.

Modifications were made to the sampling unit only (Figure 4). Initially, these modifications were confined to the impinger compartment. The intersection of the particulate and organic sample streams was in the cold impinger compartment. Condensate from wet air streams could enter the UC. The bulky UC connection flange required the elimination of two of the four impingers. The organic-sample slip stream flow-rate was determined by measuring the pressure drop across a restrictor using a sensitive Magnehelic gauge. Flow rate changes caused exaggerated gauge fluctuations.

These shortcomings were corrected by redesigning the system. The intersection of the particulate and organic sample streams was moved into the heated filter oven. A desiccant tube was placed in the oven between the intersection and the UC to remove

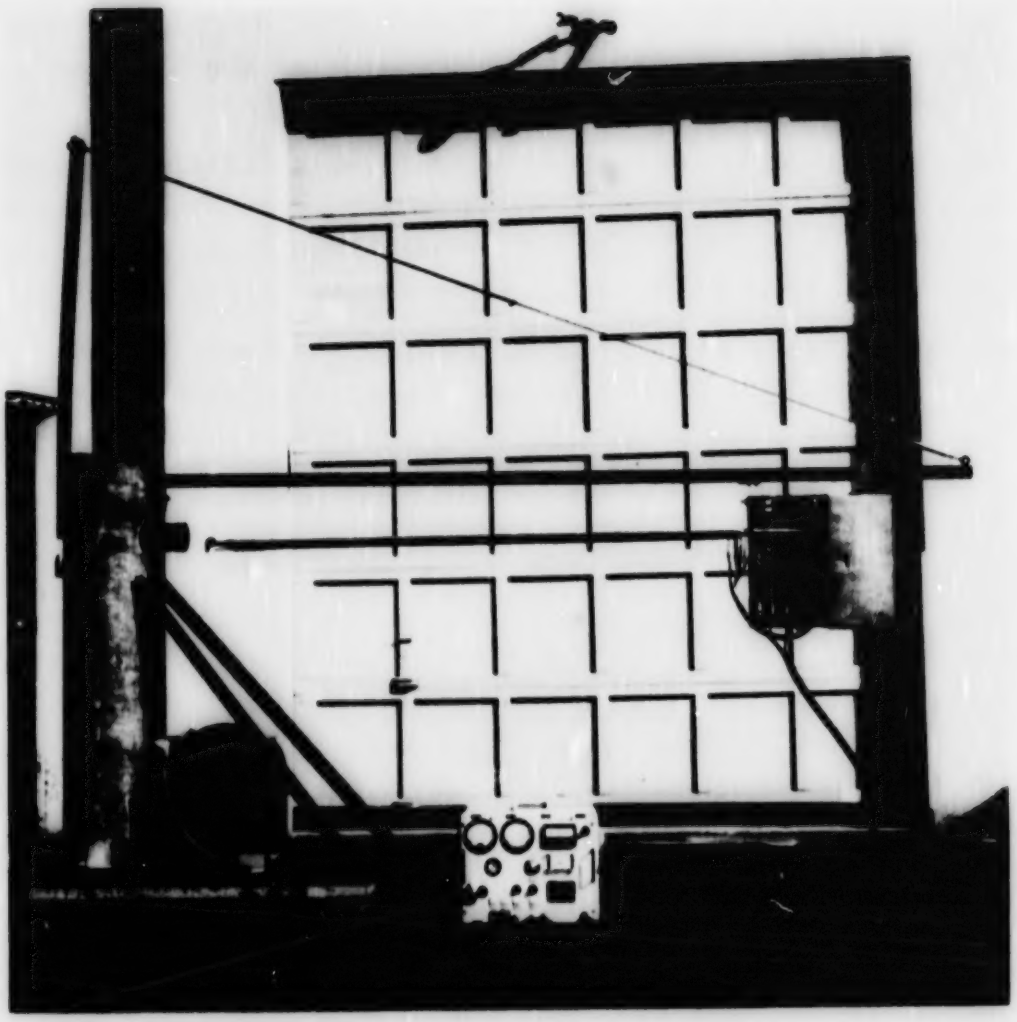


Figure 3. Joy Method 5 stack sampler

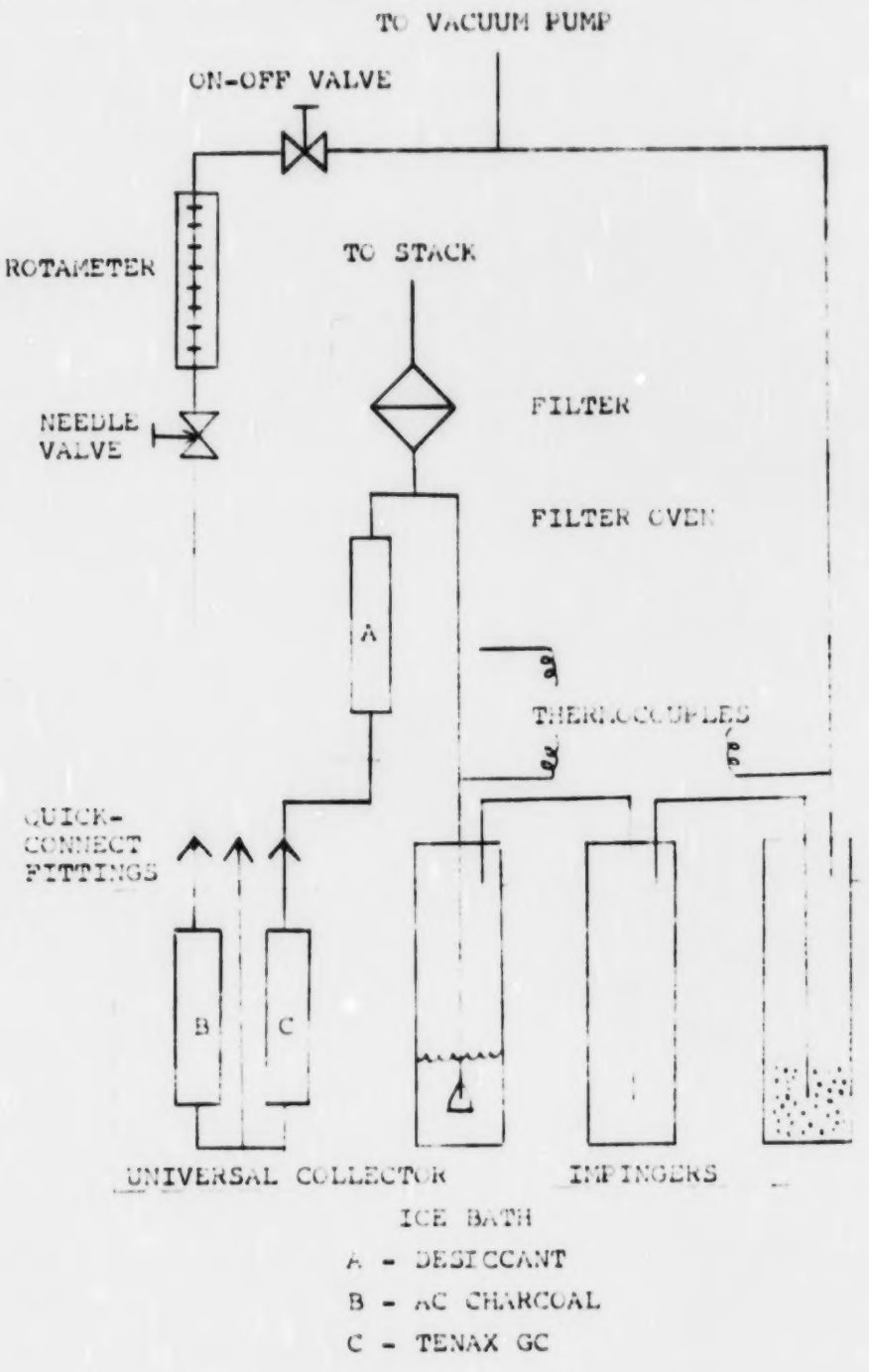


Figure 4. Schematic diagram of modified Method 5 sample train

enough water to prevent condensation. Swagelok bulkhead quick-connect fittings were installed in the wall between the filter oven and the impinger compartment. This compact design left room for three of the four standard Method 5 impingers. The three impingers and their connecting glassware were also obtained from Joy Manufacturing Company. The restrictor and Magnehelic gauge were replaced by a 15 cm Fischer and Porter Lab-Crest Model 10A1460NB22B rotameter to permit more precise flow rate determinations. Figures 5 and 6 show various views of the final sampling unit design.

CLASS ABSTRACTOR COLUMNS

For evaluation experiments, the class abstractor substrates were packed in stainless steel tubing. Swagelok brass fittings were used to connect the columns to a Perkin-Elmer 880 gas chromatograph for abstraction testing. A series of class abstractors was tested. These abstractor candidates were selected from the literature, and on the basis of past experience.

In 1963, a hydrocarbon class analyzer built for the analysis of automobile exhaust was reported.[1] The class abstractors described therein were prepared by impregnating 1 g of diatomaceous earth (80-100 mesh) with 1 ml of various solutions. The unsaturate abstractor used a 20% $HgSO_4$, 20% H_2SO_4 solution. The unsaturate and aromatic abstractor used a 4%$AgSO_4$, 95% H_2SO_4 solution.

To prepare the $HgSO_4$, H_2SO_4 solution, one adds 0.2 g of $HgSO_4$ to 0.6 ml of water in a small (5 to 10 ml) Erlenmeyer flask. The $HgSO_4$ will be yellow but highly insoluble. The mixture is then heated to incipient boiling while stirring. Enough concentrated H_2SO_4 is next added to completely dissolve the yellow $HgSO_4$ and to start the formation of a white precipitate. Water is added dropwise until the white precipitate dissolves completely. The hot solution is poured into a small Erlenmeyer flask containing 1 g of 60-80 mesh GC-22 firebrick (or the equivalent). This is mixed thoroughly until all firebrick particles are moist. The coated

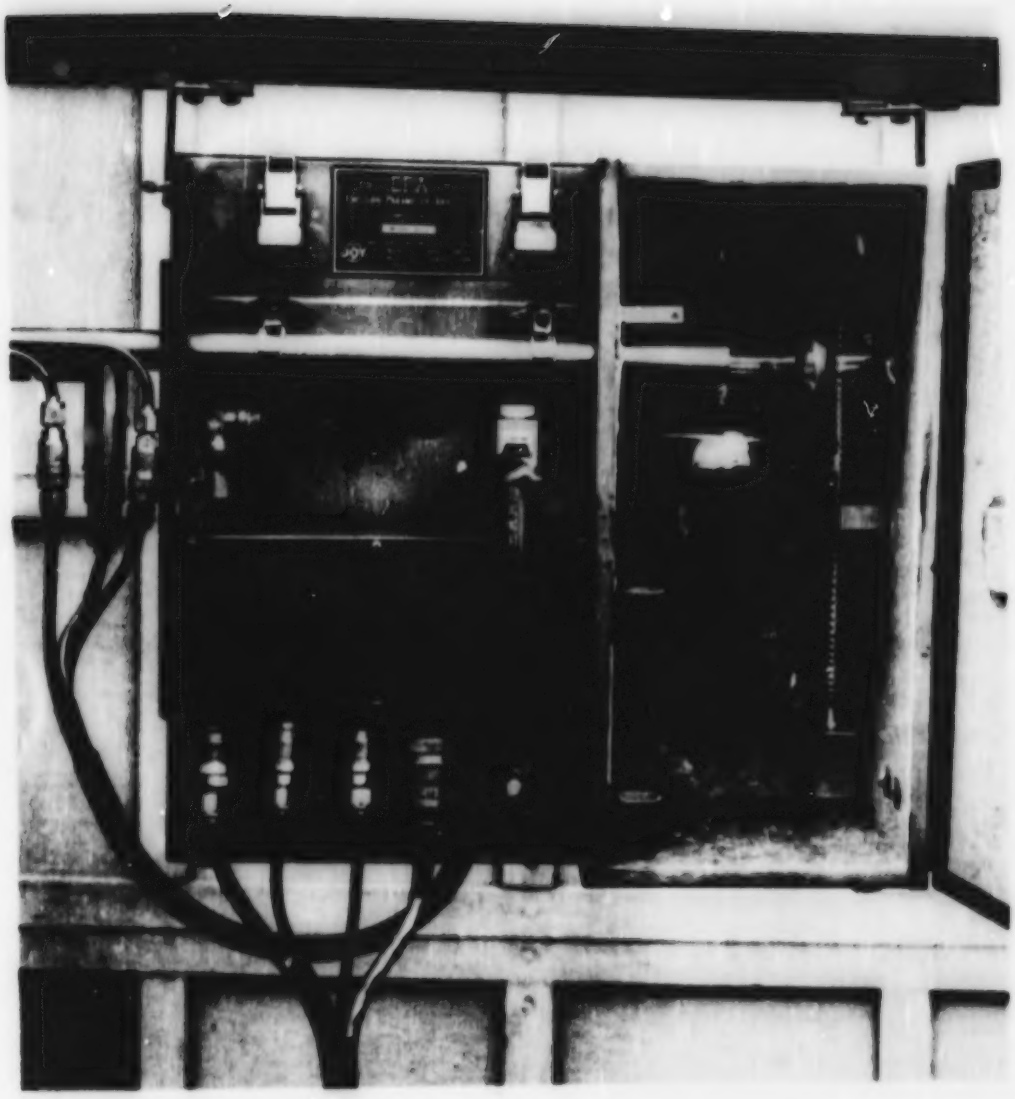


Figure 5. Front view of sampling unit

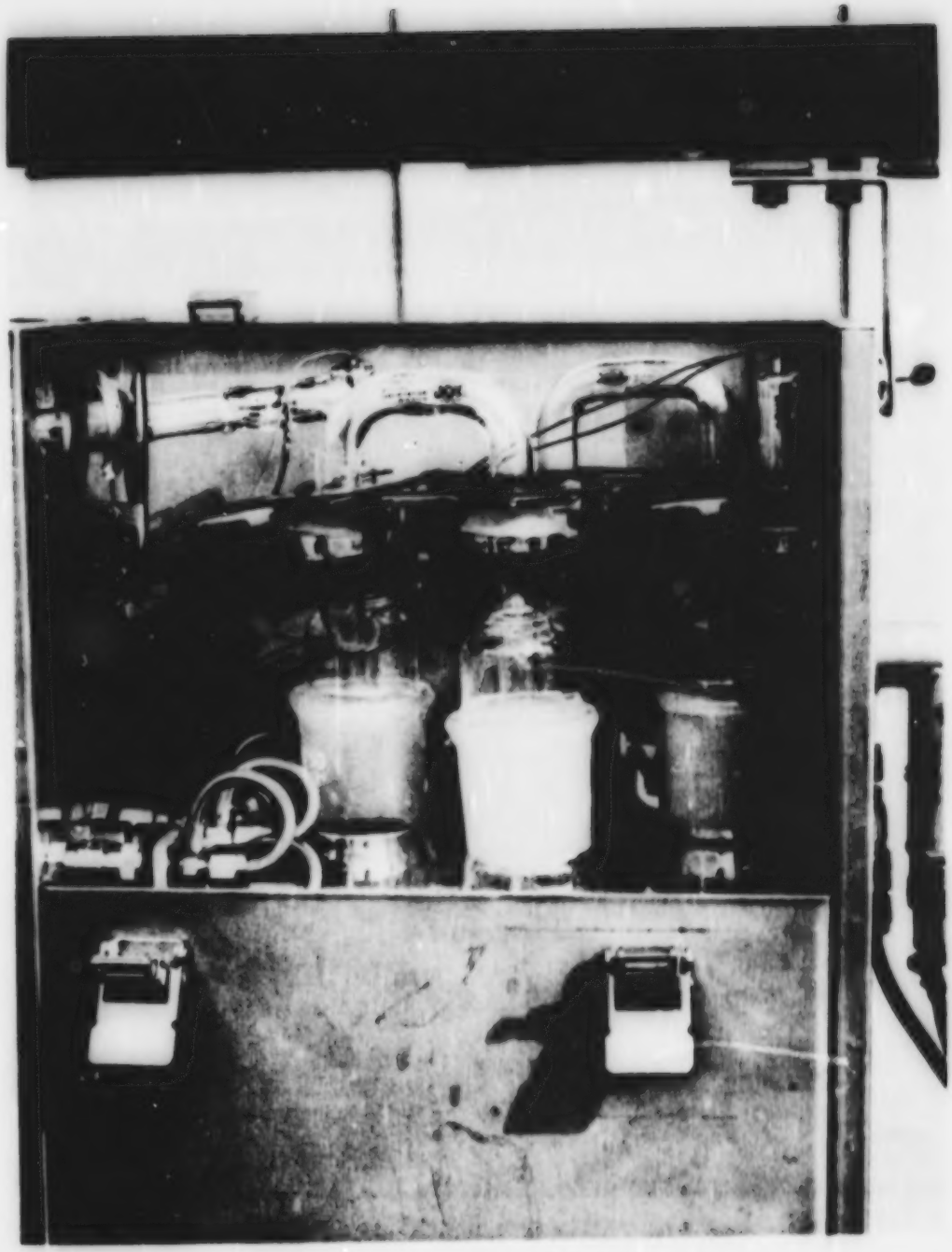


Figure 6. Sampling unit impinger compartment

firebrick is packed into a 20 by 0.64 cm O.D. stainless steel tube. The column is then conditioned under 30 ml/min helium flow at ambient temperature for 2 hours.

The Ag_2SO_4, H_2SO_4 substrate is prepared by making at least 1 ml of a solution containing 4% Ag_2SO_4, 95% H_2SO_4, and 1% water. The Ag_2SO_4 dissolves quite slowly so that continuous stirring is required to effect complete solution. A 1 ml portion of this solution is pipetted into a small Erlenmeyer flask containing 1 g of 60-80 mesh Gas-Chrom P firebrick. This is mixed thoroughly until all firebrick particles are moist. The coated firebrick is then packed into a 20 by 0.64 cm O.D. stainless steel tube. The column is then conditioned under 30 ml/min helium flow at ambient temperature for 2 hours.

Coulson used $Hg(ClO_4)_2$ and $HClO_4$ on firebrick to remove olefins and acetylenes from automobile exhaust gases as an identification method.[2] A similar abstractor was used for the analysis of gasoline hydrocarbons.[3,4] This substrate is prepared by making at least 1 g of a solution 1 M in $Hg(ClO_4)_2$ and 2M in $HClO_4$. One mixes 1 g of this solution with 1 g of 60-80 mesh Gas-Chrom P firebrick in a small Erlenmeyer flask until all firebrick particles are moist. The coated firebrick is packed into a 20 by 0.64 cm O.D. stainless steel tube. The column is conditioned under 30 ml/min helium flow at 110°C for 2 hours.

McEwen also experimented with various combinations of $Hg(ClO_4)_2$ and $HClO_4$ on firebrick for the abstraction of unsaturates from automobile exhaust gases.[5] He found that 40% $Hg(ClO_4)_2$ on GC-22 firebrick was an excellent unsaturate abstractor. This substrate is prepared by dissolving 0.8 g of $Hg(ClO_4)_2$ in about 10 ml of water in a 100 ml round bottom flask. One then adds 2 g of 60-80 mesh GC-22 firebrick to this solution. The water is removed by rotary vacuum evaporation. Again the coated firebrick is packed into a 20 by 0.64 cm O.D. stainless steel tube. The column is conditioned under 30 ml/min helium flow at 130°C for 2 hours.

Laub has suggested that a strong electron acceptor might form sufficiently strong charge-transfer complexes with electron donors, such as aromatic compounds, to provide selective abstractions.[6] A suitable electron acceptor, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), was both coated directly on a solid support and dissolved in a non-aromatic chromatographic liquid phase prior to coating.

A 10% DDQ coating on Anakrom ABS firebrick is prepared by dissolving 0.1 g of DDQ in about 5 ml of chloroform in a 100 ml round bottom flask. One then adds 1 g of 100-110 mesh Anakrom ABS. The chloroform is removed by rotary vacuum evaporation. The coated firebrick is packed into a 20 by 0.32 cm O.D. stainless steel tube and conditioned under 30 ml/min helium flow at ambient temperature for 2 hours.

To prepare a non-aromatic liquid phase containing DDQ, one saturates about 0.1 g of di(2-ethylhexyl)sebacate with DDQ. One dissolves 0.1 g of this solution in about 5 ml of acetone in a 100 ml round bottom flask. Next 1 g of 100-110 mesh Anakrom ABS is added. The acetone is removed by rotary vacuum evaporation. The coated firebrick is packed into a 20 by 0.32 cm O.D. stainless steel tube and conditioned under 30 ml/min helium flow at ambient temperature for 2 hours.

Brenner, Cieplinski, Ettre, and Coates reported[7] the adsorptive properties of various synthetic zeolites. Rowan used Molecular Sieve 5A as a class abstractor to aid in gas chromatographic identifications.[8] The molecular sieve pellets are ground and sieved to 60-80 mesh and packed in a 20 by 0.64 cm O.D. stainless steel tube. The column is conditioned under 30 ml/min helium flow at 200°C for 2 hours.

The author's past experience has indicated that salt-coated porous silica beads and aluminas possess class abstractor properties.[9,10] Both substrates are prepared in a similar manner. One dissolves the required weight of salt in about 5 ml of water in a 100 ml round bottom flask. Then 1 g of 100-150 mesh Porasil C or 100-120 mesh F-20 alumina is added. The water is removed by rotary vacuum

evaporation and the dried substrate is packed into a 20 by 0.32 cm O.D. stainless steel tube. The column is conditioned under a 30 ml/min helium flow at 300°C for 2 hours.

A boric acid-coated substrate has been found to be a quantitative abstractor of primary and secondary alcohols.[11,12] Three substrates were prepared. The first substrate is prepared by dissolving 0.4 g of Carbowax 20M in about 10 ml of chloroform in a 100 ml round bottom flask and 2 g of 60-80 mesh Chromosorb P is added. The chloroform is removed by rotary vacuum evaporation. In another 100 ml round bottom flask, 0.06 g of boric acid is combined with about 10 ml of petroleum ether and the Carbowax-coated Chromosorb is added. After the petroleum ether is removed by rotary vacuum evaporation, the substrate is packed in a 20 by 0.64 cm O.D. stainless steel tube. The column is conditioned under 30 ml/min helium flow at 225°C overnight. The preparation procedure for the second substrate is identical to the first substrate with boric anhydride substituted for boric acid. The third substrate is prepared by dissolving 0.1 g of boric acid in about 10 ml of water in a 100 ml round bottom flask. One then adds 2 g of GC-22 firebrick, removes the water by rotary vacuum evaporation, and packs the substrate in a 20 by 0.64 cm stainless steel tube. The column is conditioned under 30 ml/min helium flow at 300°C overnight.

Several substrates designed for the abstraction of oxycarbons have been reported.[12] Two of these abstractors are prepared by merely placing 100 mg of either $LiBH_4$ or $LiAlH_4$ in a short section of 0.64 cm stainless steel tubing. These columns are then ready for immediate use.

A modification of this abstractor requires coating GC-22 firebrick with $LiAlH_4$. Because $LiAlH_4$ reacts rapidly with water, precautions must be taken to prevent this reaction. To do this, one places 1 g of 60-80 mesh GC-22 firebrick in a 20 by 150 mm test tube. The firebrick is dried in a vacuum oven at 110° overnight. The firebrick is removed and sealed immediately with a stopper. When the firebrick has cooled, the stopper is quickly removed and

2 ml of a 1.3 M $LiAlH_4$ solution in diethyl ether is quickly introduced into the test tube. The stopper is replaced and the test tube agitated until all firebrick particles are moist. The stopper is again removed and a wad of glass wool inserted to cover the firebrick particles. A one-hole stopper with a glass tube inserted is then fitted to the test tube. The diethyl ether is removed by connecting a low-humidity vacuum source to the glass tube. A section of 0.64 cm stainless steel tubing is quickly packed with the coated firebrick. The column is then conditioned under 30 ml/min dry helium flow at ambient temperature for 2 hours.

CLASS ANALYZER

The final configuration of the Class Analyzer is shown in Figures 7 to 9. This breadboard system was designed and constructed to test the feasibility of the routine analysis of air samples for hydrocarbon class content.

The Class Analyzer was designed to desorb a sample from the Universal Collector. The sample is split into six streams containing selective hydrocarbon class abstractors. These class abstractors selectively remove certain hydrocarbon classes from each stream, allowing the remaining classes to pass into cryogenic traps. The trapped sample components are volatilized sequentially and swept into a hydrocarbon detector. The quantities of saturates, unsaturates, aromatics, and oxycarbons can be calculated from the detector responses to the effluents from the various class abstractor streams.

The Class Analyzer was constructed in a Bud Prestige steel cabinet type C-1552. All components are mounted on the removable 47.5 by 23 cm front panel.

The plumbing consists of 304 stainless steel tubing and Swagelok brass fittings. Teflon tubing is used to connect the Class Analyzer to the FID. The main needle valve and all on-off valves are Whitey valves. The individual stream needle valves are integral

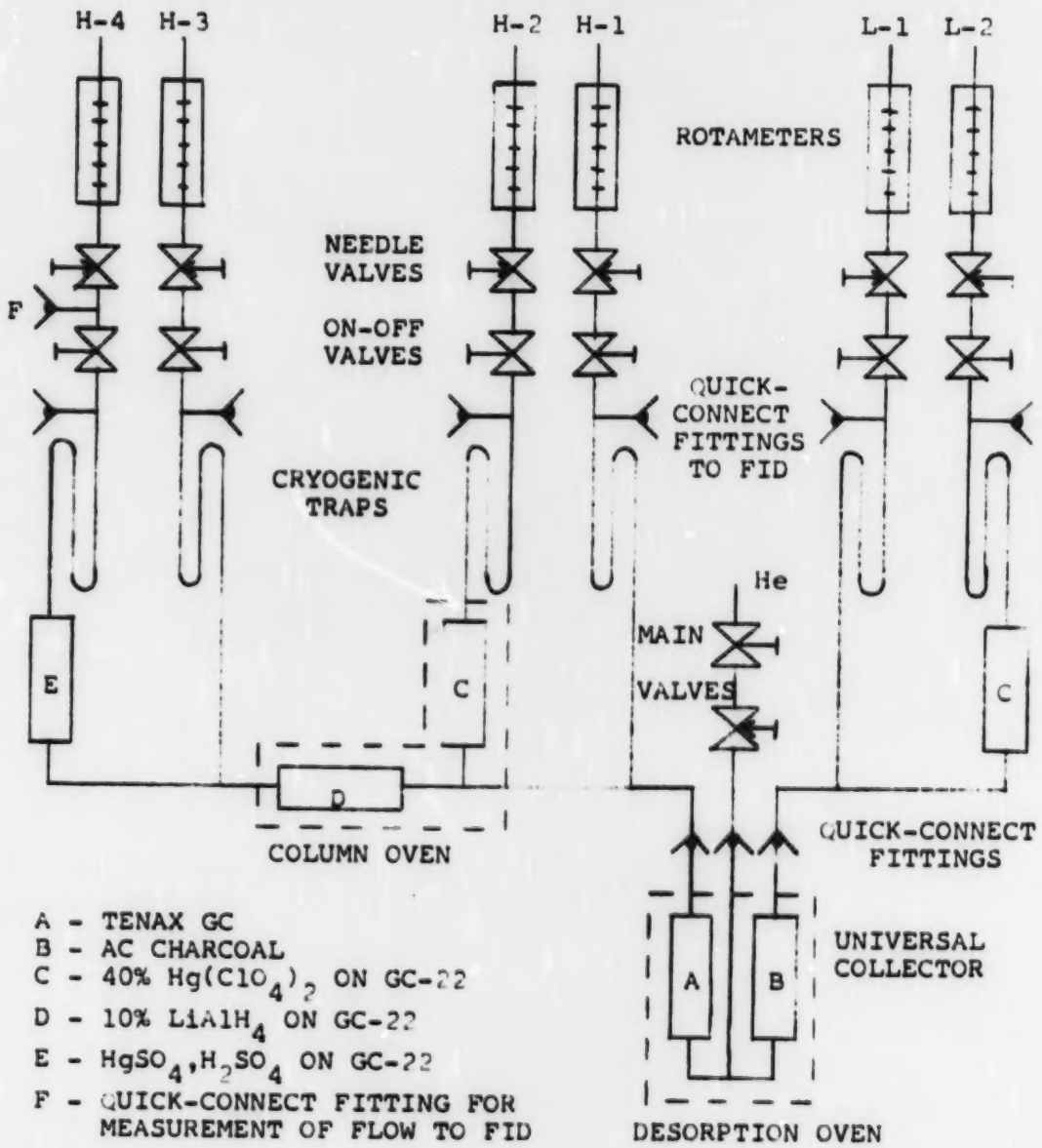


Figure 7. Schematic diagram of Class Analyzer

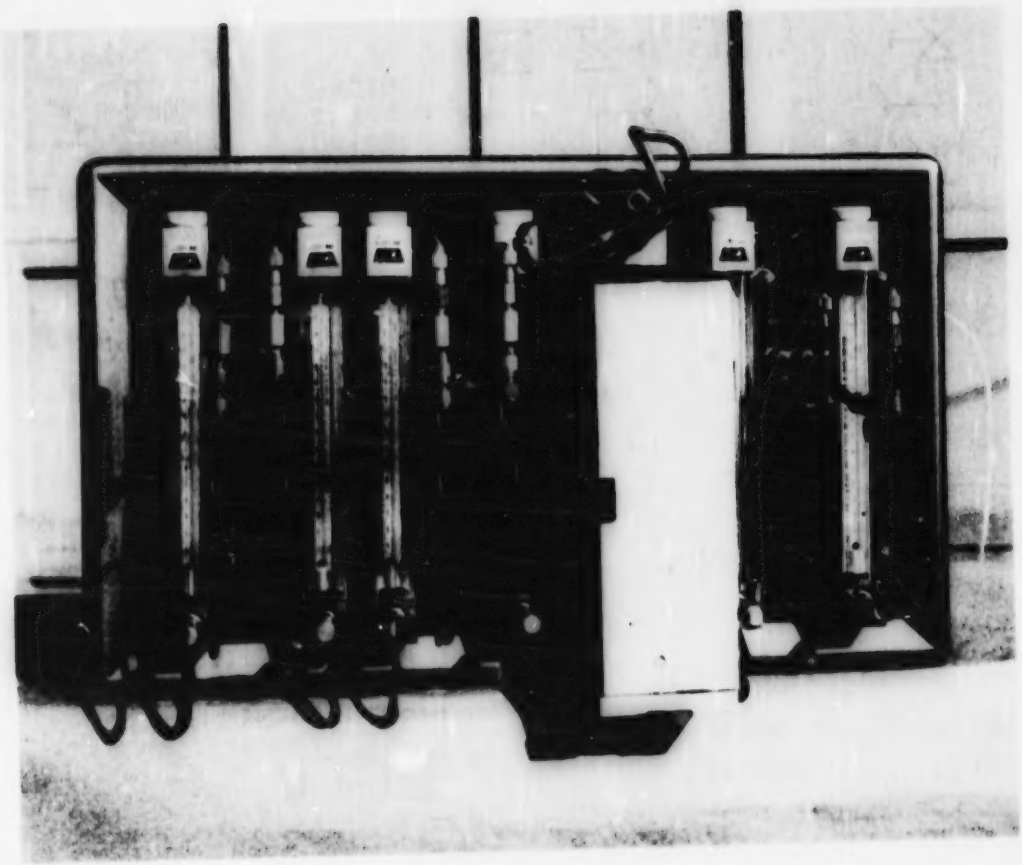


Figure 8. Front view of Class Analyzer

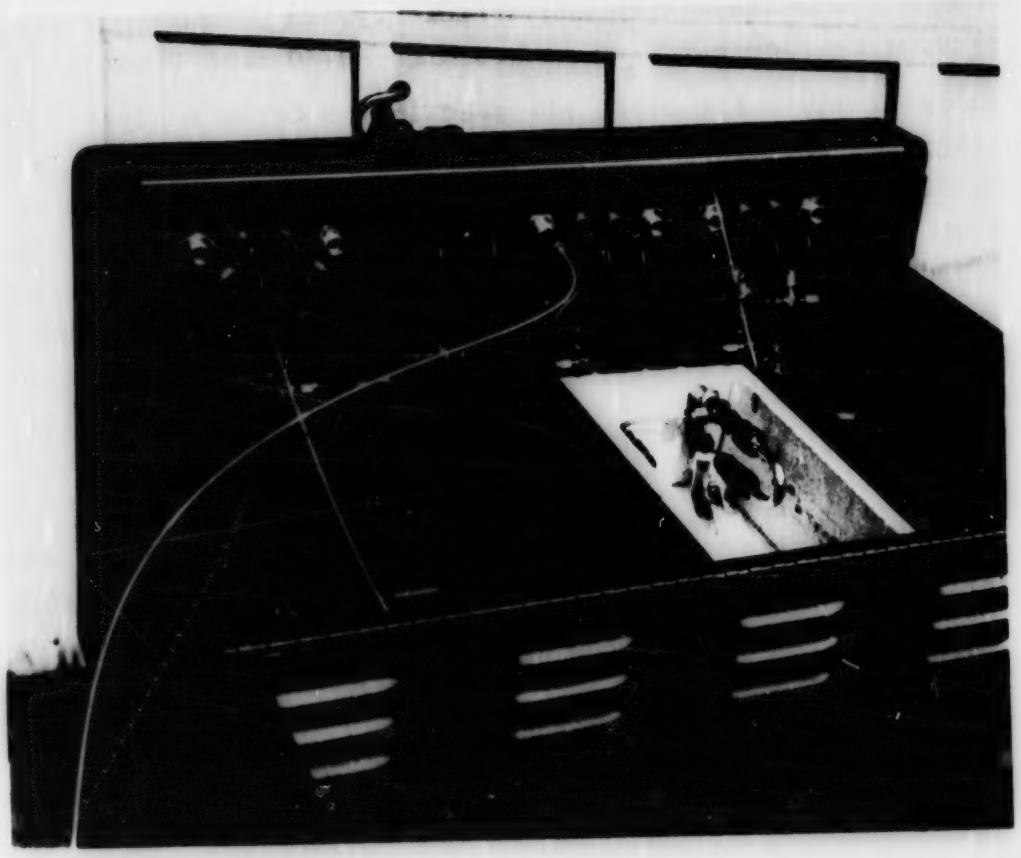


Figure 9. Rear view of Class Analyzer

parts of the 15 cm Fischer and Porter Lab-Crest 10A1460NB22B rotameters. These rotameters are equipped with black glass floats which provide a measurement capability of 0 to approximately 55 ml/min of helium. Swagelok quick-connect fittings are used for connecting the UC to the Class Analyzer and for connecting the Class Analyzer to the external FID.

The cryogenic traps are of the "race track" design. The heavy-ends traps are 0.32 cm 304 stainless steel tubing. In order to enhance the methane trapping efficiency, the light-ends traps are 0.32 cm copper tubing packed with 60-80 mesh Devarda's metal.[13]

Two specially-built ovens are used in the Class Analyzer. The UC desorption and class abstractor ovens are heated to 200° and 125°, respectively, by resistance elements. Oven temperatures are adjusted by means of standard laboratory autotransformers and measured with laboratory thermometers. The UC desorption oven has a hinged door to permit easy attachment and removal of the UC. The class abstractor oven top is removable for class abstractor substrate replacement.

LABORATORY TEST STACK

A laboratory test stack was designed and constructed to permit testing of the modified stack sampler in the lab (see Figure 3). The stack itself is a 152 by 30 cm section of galvanized pipe. A short section of 8.9 cm pipe was welded to a hole in the side of the stack to serve as a test port.

A high-capacity squirrel cage blower provides stack air flow which is varied by restricting the blower inlet area. The entire stack and blower assembly was mounted on a mobile structural frame.

SECTION V

EXPERIMENTAL PROCEDURES

UNIVERSAL COLLECTOR EVALUATION

The various UC candidates described in Section IV were evaluated for their performance characteristics. The UC test apparatus (see Figure 1) was employed for these evaluations.

The evaluation procedure involved the installation of a candidate column in the gas chromatograph oven. After column preconditioning, the temperature of the candidate column was maintained at either 30° or 0°. The column by-pass valve was opened to permit the carrier gas (nitrogen) to flow directly to the FID. When a stable recorder baseline was established, the nitrogen was turned off and a dilute (ca. 50 ppm) stream of hydrocarbon-containing gas was introduced, also at 30 ml/min. The detector amplifier attenuation was adjusted so that the recorder pen position was at a maximum while remaining on scale. Then the nitrogen flow was restored and the by-pass valve turned off to force the carrier gas flow through the column.

When a steady recorder baseline was again established, the dilute hydrocarbon gas was then passed into the column. After the hydrocarbon was detected by causing a recorder pen deflection, the nitrogen flow was restored causing the recorder pen eventually to return to the baseline. The volume of gas which flowed from the time the dilute hydrocarbon stream was turned on until the first detectable pen deflection occurred was the breakthrough volume for that particular hydrocarbon. Because this evaluation procedure was intended to establish comparisons between various UC candidates, the system void volume could be ignored as a common factor.

The desorption volumes were then determined at 200°. The candidate column was filled to just under its breakthrough volume with a hydrocarbon sample at 30° or 0°. The sample flow was turned off and the column heated to 200°. Then the backflush valve was turned to reverse the gas flow through the column. The nitrogen carrier gas was

turned on. The desorption volume was the volume of carrier gas which flowed through the column from the time the carrier gas was turned on until the recorder pen returned to its baseline.

The hydrocarbons used for UC candidate evaluation were approximately 50 ppm mixtures of methane, hexane, benzene, and ethanol, each in nitrogen. These hydrocarbons represented a range of class types and boiling points. The determination of the methane breakthrough volume for the final configuration of the UC was performed by substituting the UC for the trap in the test apparatus. The column by-pass valve was opened and the trap valve positioned so that gas flowed through the UC before entering the FID. The UC was submerged in an ice bath and various methane mixtures (ca. 25-2500 ppm) introduced into the system. The methane breakthrough volume was then determined as previously described.

BREAKTHROUGH DETECTOR EVALUATION

The Laboratory Data Control, Inc. piezoelectric detector was tested for its sensitivity to methane. The test procedure involved establishing a steady baseline flowing 30 ml/min of nitrogen through the detector. Then the nitrogen was turned off and the methane mixture turned on also at 30 ml/min. A standard 45 ppm mixture of hexane in nitrogen was also used as a test gas.

CLASS ABSTRACTOR CANDIDATE EVALUATION

Early class abstractor evaluation was performed by merely installing a candidate column in a Perkin-Elmer 880 gas chromatograph and injecting a series of model compounds into the column to determine whether abstraction occurred. The test apparatus was modified for later candidate evaluation to allow the detection of partial abstraction situations (Figure 10). Comparing the detector response to a model compound first injected into an open tube leading to the detector followed by an identical injection into the abstractor candidate column gave a better indication of abstractor performance. Whenever possible, the detector response was integrated by an Autolab System I computing integrator.

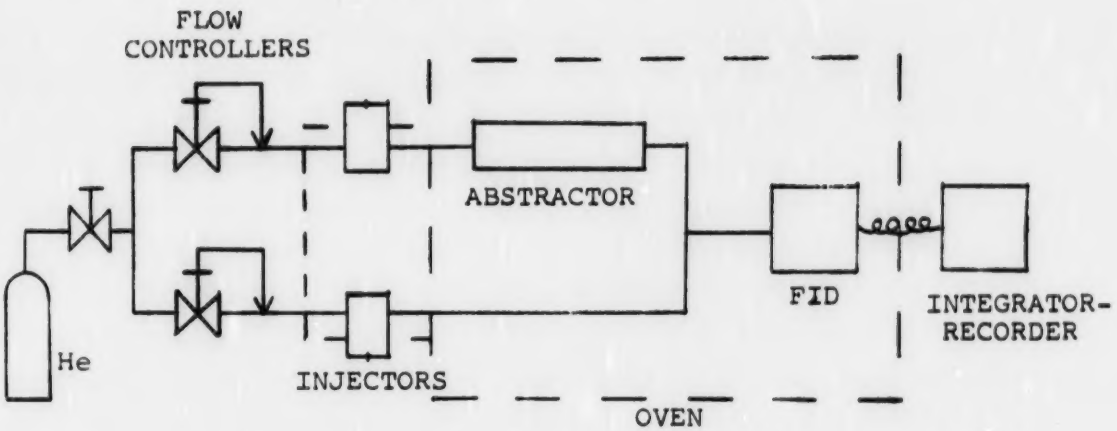


Figure 10. Schematic diagram of class abstractor test apparatus

Table 1 is a list of model compounds which were used for most of the abstractor candidate evaluations. For each class, representatives of low and higher boiling compounds were selected. In some cases, additional compounds were used as models to better define the performance of a particular abstractor candidate.

CLASS ANALYZER EVALUATION

The performance of the Class Analyzer was evaluated using known samples. With the UC by-pass (Figure 11) connected to the Class Analyzer, samples were injected with a syringe.

In order to measure sample recovery percentages and abstraction efficiency, the effluent from the Class Analyzer was directed to the FID in an Aerograph Hy-FI Model 600-B gas chromatograph. The FID was also connected to the chromatograph injector by an open tube. This arrangement permitted the injection of a sample directly into the FID so that a specific detector response could be determined. An identical injection into the Class Analyzer produced a detector response which could be compared with the specific response measured previously. Any reduction in response could be attributed to sample loss. Whenever possible, the detector response was integrated by an Autolab System I computing integrator.

LABORATORY TEST STACK

The laboratory test stack was used to introduce synthetic samples to the stack sampler. Gaseous samples were introduced directly into the blower inlet at a controlled flow rate. Liquid samples were infused into a glass fiber wick placed in the blower inlet. An adjustable speed Sage infusion pump drove a 10 ml syringe containing the sample. The air stream flowing over the wick evaporated the sample. The air flow was adjusted to about 6700 l/min by restricting the blower intake area to 64 cm^2.

The usual procedure observed involved positioning the stack sampler inlet nozzle in the center of the stack diameter. The stack blower and stack sampler pump were turned on and sample introduction begun.

Table 1. MODEL COMPOUNDS FOR CLASS ABSTRACTOR EVALUATION

Class	Model compounds
Saturate	Methane, hexane
Unsaturate	Ethene, 1-octene
Aromatic	Benzene, 1,2,4-trimethylbenzene
Halocarbon	Chloroform, 1,1,2,2,-tetrachloroethane
Oxycarbon	Methanol, 4-methylbutanol
	Acetaldehyde, 2-ethylhexanal
	Acetone, cyclohexanone
	Ethyl acetate, isopentyl acetate
	Diethyl ether, tetrahydrofuran

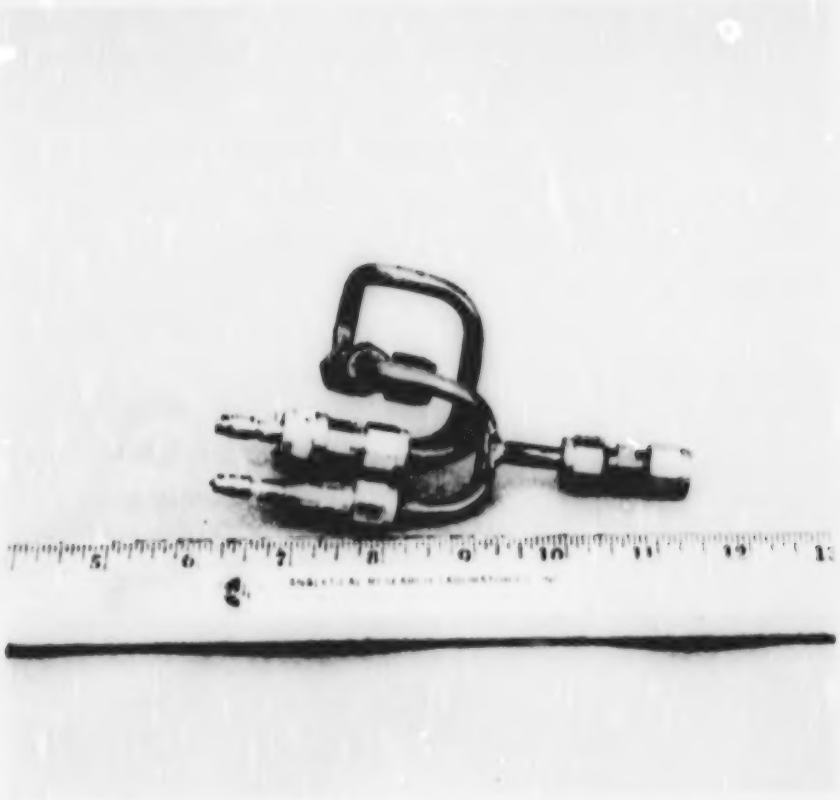


Figure 11. Universal Collector by-pass

An equilibration period was allowed before sample collection began to ensure the most constant sample concentration possible. Grab samples were collected immediately before and immediately after sampling. The contents of the stainless steel bombs used for grab sampling were analyzed by gas chromatography in order to characterize the sample.

The samples, which were collected in 6 UC's, were then analyzed by the Class Analyzer. Multiple samples were collected to determine the analytical precision. The accuracy of the sampling and analytical methods was determined by comparing the results with those obtained from the gas chromatographic analysis of the grab samples.

MODIFIED STACK SAMPLER AND CLASS ANALYZER

The operating procedures for the modified stack sampler and the Class Analyzer are described in their respective Operation Manuals.

SECTION VI

DISCUSSION

LITERATURE SURVEY

An extensive literature survey was completed prior to the beginning of the technical effort. The subjects sought were based on two-step sampler-analyzer design. The first step provides for the collection of total organic emissions while the second step provides for the separation of the collected sample into chemical classes.

Because the total collection of the sample must be nondestructive, emphasis was placed on obtaining information on available solvents whose adsorption mechanism is based on physical processes.

The separation of the collected sample into chemical classes, on the other hand, needs not exclude selective sample destruction. Hence, in seeking unique means of trapping a specific chemical class without collecting other chemical species, both physical and chemical means were investigated. Again, sorbents were sought as class abstractors. The headings of chemisorption and analytical means of determining specific classes of compounds were searched. Principal interest in specific class determinations was focused on saturates, olefins, aromatics, halocarbons, alcohols, ketones, aldehydes, esters, ethers, mercaptans, and carboxylic acids.

The pursuit of pertinent information followed several pathways. For current journal publications (1971 to present), a computer search was requested through NASA's Western Research Application Center (WESRAC) at the University of Southern California. This search was based on key word indexing of Chemical Abstracts. An additional search, covering principally government publications, was requested through the Commerce Department's National Technical Information Service (NTIS) facilities. However, NTIS felt that their survey would not be productive because of our subject matter, so the survey request was cancelled.

Our own personnel conducted a survey of literature up to 1971 by use of Chemical Abstracts cumulative indices and Air Pollution Abstracts. Because cumulative indices were available through 1971, computerized searching of earlier titles would have been less economical than a personal one.

The literature survey produced about 80 pertinent references. These references were obtained and studied to determine their applicability to the present effort.

UNIVERSAL COLLECTOR

Ideally, the Universal Collector (UC) is a device which will quantitatively collect all volatile organic compounds from a stationary source. The UC will store these collected organic compounds without sample decomposition. The sample can then be quantitatively released from the UC with no contamination added to the sample by the UC itself. Finally, the UC should be a compact device.

Past experience and information from the literature survey indicated that no single sorbent could fulfill the requirements of an ideal UC. Typical gas chromatographic sorbents do not have sufficient capacity for the more volatile organic compounds (light ends), such as methane. Highly active adsorbents such as activated charcoal have a high capacity for the light ends but the less volatile organic compounds (heavy ends) are irreversibly adsorbed. Therefore, the envisioned UC was a dual-bed unit: an active adsorbent to remove the light ends preceded by a sorbent whose purpose is to prevent the heavy ends from reaching the more active adsorbent.

The evaluation procedure for the various UC sorbent candidates approximated the proposed operating conditions for the UC. Sample collection (sorption) was to occur at ambient or ice-bath temperature. Sample release (desorption) was to occur at an elevated temperature (ca. 200°C) to ensure rapid and complete desorption.

Past experience and the results of the literature survey indicated the existence of a variety of suitable candidates for the heavy ends

sorbent. The relatively stable, inert surface of a porous organic polymer seemed to be ideal.

By far the most common type of porous polymer sorbent is a cross-linked polymer produced, for example, by copolymerizing styrene and divinyl benzene. This group is represented by the Porapak series (Waters Associates) and the Chromosorb Century series (Johns-Manville Corp.). The different properties of members of each series are due to variations in pore size, surface area, and chemically-bound functional groups. Porapak Q was chosen as a representative of that sorbent type because it is widely used as a gas chromatographic support for the analysis of hydrocarbon mixtures.

The sample capacity of these porous polymer supports can usually be increased by coating the surface with a suitable chromatographic liquid phase. This liquid phase should have a negligible vapor pressure to prevent the contamination of the collected sample by the liquid phase. A liquid phase which has the necessary properties is OV-1, a methyl silicone gum with a recommended maximum temperature limit of 350°C. A 3% coating (by weight) was applied on 80-100 mesh Porapak Q.

A porous polymer that is significantly different from both the Porapak and Chromosorb Century series is Tenax GC. This support is a polymer based on 2,6-diphenyl-p-phenylene oxide. It is more thermally stable than any members of the Porapak or Chromosorb Century series. No significant volatilization occurs below 320°. Zlatkis has demonstrated its usefulness in trapping volatile constituents of urine, human breath, automobile exhaust, ambient air, and etc.[14]

The results of the experimental evaluation of the heavy end sorbents are summarized in Table 2. Coating Porapak Q with OV-1 does indeed increase the capacity of the sorbent. However, both the retention and desorption volumes are increased. The disadvantage of an increased desorption volume largely cancels the increased

Table 2. CANDIDATES FOR HEAVY ENDS SORBENT OF UNIVERSAL COLLECTOR

Sorbent	Sorbate	Specific retention volume (temperature), ml/g (°C)		Specific desorption volume at 200°C, ml/g
Porapak Q	Methane	6.2	(30)	-
	Hexane	161.	(100)	43
		>6550.	(30)	-
	Benzene	193.	(100)	50
		>8510.	(30)	-
	Ethanol	213.	(100)	65
		> 7340.	(30)	-
3% OV-1 on Porapak Q	Methane	5.7	(30)	-
	Hexane	201.	(100)	108
	Benzene	231.	(100)	101
		> 6000.	(30)	-
	Ethanol	260.	(100)	92
Tenax GC	Methane	30.	(0)	-
	Ethane	79.	(0)	-
	Propene	578.	(0)	-
	Butane	167.	(0)	-

retention volume. The possibility of sample contamination by the OV-1 coating makes this support somewhat inferior to uncoated Porapak Q.

Inspection of Porapak Q after repeated temperature cycling from ambient to 200° revealed a change in its color from white to brown. Although its sorptive properties did not appear to deteriorate, its long-term performance was subject to suspicion.

Tenax GC performed well in all tests. It has sufficient capacity to prevent heavy ends from reaching the light ends sorbent. Its thermal stability seems to be excellent with no signs of deterioration after several months' usage. Therefore, Tenax GC was selected as the heavy ends sorbent.

Selecting the light ends sorbent was a more difficult job than the heavy ends sorbent. The quantitative retention of lower hydrocarbons, such as methane, requires an extremely active surface. Normal gas chromatographic supports are not acceptable. Past experience with aluminas and silicas indicated that these sorbents would be inferior to charcoals and molecular sieves for the retention of methane.

The eight charcoals and molecular sieves shown in Table 3 were selected for experimental evaluation because of past experience with them or because of advantageous properties claimed for them. Most of these materials are not designed for chromatographic applications. They are manufactured as pellets which required grinding and sieving to produce the proper size particles (ca. 60-100 mesh).

The Linde Molecular Sieves are synthetic zeolites. The numerical designation (4A, 5A) is related to the approximate diameter (in angstroms) of the pores in the open zeolite structure. The AW-500 molecular sieve has been treated by acid washing.

Barnebey-Cheney AC charcoal has been used by NASA in the air purification systems of manned spacecraft. Both the AC and GI type charcoals have demonstrated exceptionally high capacities for

Table 3. CANDIDATES FOR LIGHT ENDS
SORBENT OF UNIVERSAL COLLECTOR

Sorbent type	Sorbent	Specific retention volume of methane at 30°C, ml/g
Molecular sieve	Linde AW-500	5.3
	Linde 4A	3.2
	Linde 5A	4.9
Activated carbon	Barnebey-Cheney AC	85.
	Barnebey-Cheney GI	46.
	Nuchar WV-H	6.8
	Cabot Graphon	6.7
	Carbosieve-B	4.5

organic compounds. Nuchar WV-H is a controlled porosity charcoal whose capacity for specific organic compounds was unknown to the project. Graphon is a charcoal with a highly uniform, graphitized surface. Carbosieve-B is a controlled porosity charcoal which is claimed to have properties similar to molecular sieves.

Methane retention at 30° was determined by introducing a 50 ppm mixture of methane in nitrogen into a 20 by 0.64 cm O.D. stainless steel tube filled with the test sorbent. The instant that methane breakthrough was detected determined the retention volume. The specific retention volumes were calculated by dividing the actual retention volumes by the weight of sorbent used for each test. Barnebey-Cheney AC charcoal clearly had the highest specific retention volume.

The two preferred sorbents, Tenax GC and AC charcoal, were arranged in series for sample collection (Figure 12a). However, special requirements for the separation and cryogenic trapping of the light ends necessitated keeping the light and heavy ends separated during sample recovery. Thus, a third port was installed in the UC for the introduction of a carrier gas during sample recovery (Figure 12b).

The capacity of the UC was of critical importance. Sensitivity of the analytical technique would suffer if the capacity were too low. Maintaining the UC at 0° during sample collection and incorporating the greatest practical amount of sorbent would maximize the capacity. Packing each sorbent in a 20 by 0.95 cm O.D. stainless steel tube results in sufficient capacity. This permits about 2.8 g of Tenax GC and 6.6 g of AC charcoal to be used in each UC. Methane breakthrough does not occur until over 400 ml of sample have passed through the UC.

A convenient means of attaching the UC to the stack sampler and the Class Analyzer required careful consideration. The UC ports must be closed when the UC is not connected to either the stack sampler or the Class Analyzer. This prevents sample contamination or loss.

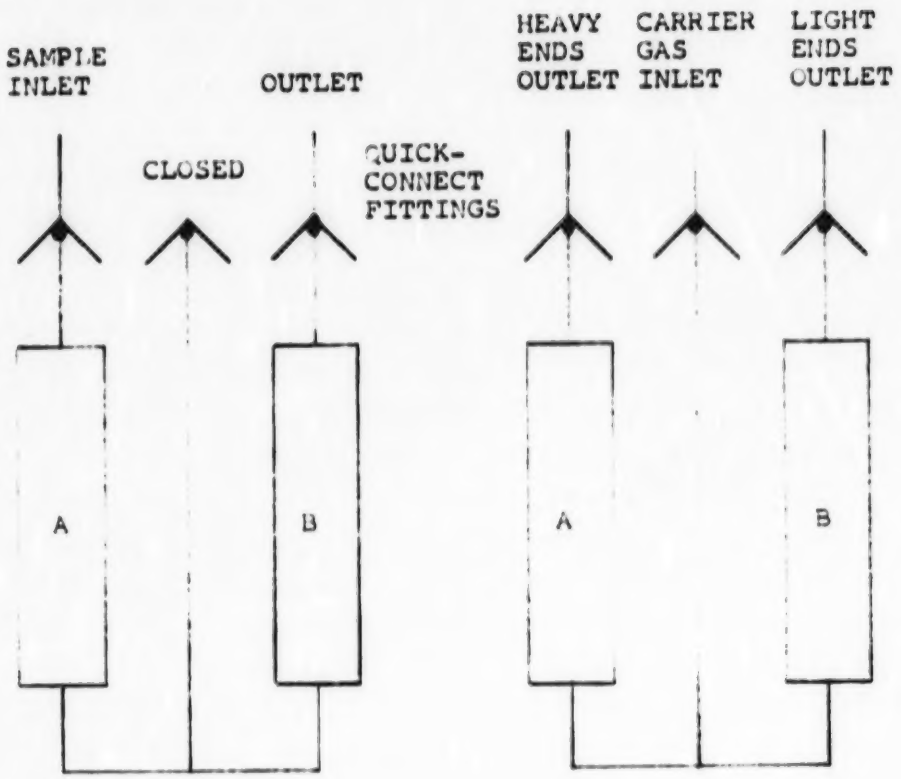


Figure 12. Schematic diagram of Universal Collector

Initially, a threaded flange was designed and made as the connector for the UC. This flange was somewhat bulky and expensive. It did not provide automatic shut-off of the UC ports.

The next connector design tested incorporated individual double-ended automatic shut-off quick connect fittings. Two disadvantages of this system do exist. Some sample loss or contamination can result due to the Buna-N O-rings which are used in the fittings. Also, perfect alignment of the three fittings on each UC with the fittings on the stack sampler and Class Analyzer is difficult. This causes more difficulty in connecting the UC than is desirable. However, the system does work and is the best alternative found to the present time.

STACK SAMPLER

The modifications made to the Joy Manufacturing Company Method 5 stack sampler have converted a particulate sampler into a sampler capable of collecting volatile hydrocarbons as well as particulates in stack gases. The UC capacity and the hydrocarbon sample train flow rate capabilities permit a 400 ml stack gas sample to be collected in a minimum of 7 minutes and a maximum of about 230 minutes. Replacement of a saturated UC with an empty one requires less than 15 seconds, so the actual maximum sampling period depends on the number of UC's available for sample collection. Therefore, both short-term and long-term sampling can be consecutively performed during the same test-period on site.

One possible problem might occur during the sampling of hot, humid stack gases. Condensation of water vapor in the UC could occur. Excess moisture can cause a loss of hydrocarbon capacity. A desiccant tube has therefore been installed upstream of the UC in the filter oven. The literature indicates that anhydrous potassium carbonate is a desiccant which does not abstract most hydrocarbons.[15,16] However, the project staff did not have an opportunity to test potassium carbonate for its inertness toward hydrocarbons and its efficiency as a desiccant at the 120°C temperature of the filter oven. Therefore, further work needs to be done in this regards.

Incorporation of a breakthrough detector downstream of the UC in the hydrocarbon sample train was planned. The purpose of this detector was to alert the operator when any hydrocarbon eluted from the UC.

The performance characteristics required of the breakthrough detector were quite demanding. The detector had to be capable of detecting methane in the low ppm range. Inorganic compounds would have to be nonresponsive. It had to be compact, rugged, and capable of operating in the field.

A flame ionization detector (FID) has the necessary sensitivity properties. Operation of a FID in the partial vacuum of the stack sampler train would be inconvenient. Providing sources of pure hydrogen and air would be difficult. A small, portable hydrogen generator could not be found.

A thermal conductivity detector (TCD) is compact, portable, and rugged, but detects inorganic as well as organic compounds. Its sensitivity is greatest when a carrier gas with a thermal conductivity greatly different from the sample compounds is used. Air is a poor carrier gas in this respect.

International Sensor Technology of Costa Mesa, California, developed a solid state electrolytic cell hydrocarbon gas sensor. The conductivity of the solid electrolyte changes when hydrocarbon gases are adsorbed on the electrolyte surface. Unfortunately, gas flow over the electrolyte cannot be tolerated. Diffusion of the sample to the detector is the required mode of operation. A major drawback of this device was its ultimate sensitivity to methane. Response to 100 ppm methane was assured, but no experience with lower levels was available.

Laboratory Data Control (LDC) of Riviera Beach, Florida, has developed a piezoelectric detector. The detector is a quartz crystal oscillating at about 10 MHz. A thin layer of a suitable gas chromatographic liquid phase is coated on the crystal. When a sample

passes over the coated crystal, organic components dissolve in the liquid coating increasing the crystal mass and lowering its oscillating frequency. Because this is a mass detector, heavier compounds are more easily detected. Nevertheless, LDC saw no problems meeting our sensitivity requirements.

Because the piezoelectric detector seemed to be the most promising candidate breakthrough detector available, one was purchased as part of a complete, although inexpensive gas chromatograph. Operation of the detector on either 115 VAC or 12 VDC did not affect its performance. Operation of the detector at 0° rather than ambient temperature did not cause any problems and may have even improved its sensitivity somewhat. Sensitivity was further increased by using a 1 mv rather than a 10 mv recorder. However, the increase in background noise partially nullified the sensitivity increase.

Initially, the crystal was coated with Carbowax 400, a polyethylene glycol. A mixture of 45 ppm hexane in nitrogen was detectable, but not without operating at the lower attenuation settings. More sensitivity would be required for the detection of low levels of methane.

During experimentation, the crystal oscillation ceased, probably due to irreversible crystal surface contamination. The crystal was cleaned and recoated with Carbowax 400. Obtaining the proper coating thickness was a trial-and-error process. The crystal cracked before an optimum coating layer could be deposited.

A new crystal was obtained from LDC. In order to improve the detector sensitivity toward methane, LDC suggested a crystal coated with SE-30, a silicone gum rubber. This new detector was thermally insulated to minimize baseline drift.

With the new crystal, a 45 ppm mixture of hexane in nitrogen (mixed and analyzed by The Matheson Company) flowing at 30 ml/min at 25° produced at 0.49 mv signal at an attenuation of 16. According to theory, the piezoelectric detector response is proportional to concentration, molecular weight, and the partition coefficient of the sample in the crystal coating. Based on empirical chromatographic

data, the detector response to a 45 ppm methane mixture should have been about 650 times less than for a comparable hexane sample. The resulting signal, 0.012 mv at an attenuation of 1, is less than the noise level. The response of the detector to synthetic mixtures of methane in nitrogen in the 30 to 100 ppm range was independent of the methane concentration.

In a continuing effort to gain the required sensitivity, LDC factory technical representatives and Dr. David Bonner, a piezoelectric detector specialist at Texas Tech University, were consulted. Detection of hydrocarbons lighter than hexane has not been investigated. Therefore, we concluded that a considerable research effort would be required to obtain sufficient methane sensitivity. It was decided, therefore, to eliminate the piezoelectric detector from consideration as a possible breakthrough detector during the present effort.

Our research direction was accordingly changed to determine whether a breakthrough detector was really required. The breakthrough volumes of methane samples ranging from 25 to 7500 ppm were determined. The breakthrough volume from the UC at 0^{o} and 50 ml/min flow rate remained constant at about 425 ml. Therefore, if sample sizes are kept below 400 ml, no breakthrough should occur under any circumstances. This is true because the UC operates by a reversible adsorption mechanism. Therefore, the breakthrough volume is unaffected by past exposure to organic molecules because essentially all molecules will eventually elute. By establishing a set of sampling conditions, premature breakthrough can thus be avoided.

CLASS ABSTRACTORS

The central goal of this research effort is to develop a method of analyzing a gaseous sample for its content of saturates, unsaturates, aromatics, halocarbons, and oxycarbons. The approach we have chosen is to assemble a series of chromatographic columns which selectively abstract certain hydrocarbon classes.

The ideal class abstractor column quantitatively abstracts a class (or classes) of hydrocarbons. Those classes which are not abstracted should pass through the column without being retained. Because the abstracted compounds accumulate in the column, a simple regeneration of the column would be ideal.

Table 4 lists the 17 different abstractor candidates which were evaluated. Most of these substrates consist of materials coated on solid supports. With the exception of the Molecular Sieve (synthetic zeolites), the Porasil (porous silica), and the alumina, all supports are some form of calcined diatomaceous earth. The GC-22 and Chromosorb P are diatomaceous earths which have been calcined without a flux. They generally have a larger surface area and are more adsorptive and efficient than those diatomaceous earths which have been calcined with a sodium carbonate flux. Gas-Chrom P is flux calcined, washed with acid to remove inorganic impurities, washed with base to remove organic impurities, and washed with water until neutral. Anakrom ABS is similar to Gas-Chrom P except that it has been deactivated and made hydrophobic by silanization with dimethylchlorosilane.

These treatment procedures are designed to improve chromatographic peak shape, resolution, etc. Such considerations are unimportant for a class abstractor. Therefore, the results would probably remain identical had all diatomaceous earth supports been the same. The use of different supports merely reflects the preference of each research group that published its work with a certain substrate.

A substrate designed to abstract unsaturates and aromatics, Ag_2SO_4, H_2SO_4 on Gas-Chrom P[1], was unsatisfactory for use in the Class Analyzer. Oxycarbons and certain unsaturates were abstracted, but aromatics were merely retained strongly at 30°. Two separate substrate preparations were made with no appreciable difference in performance.

An unsaturate abstractor, $HgSO_4$, H_2SO_4 on GC-22[1], abstracted all unsaturates tested with the exception of ethene. Oxycarbons were

Table 4. CLASS ABSTRACTOR CANDIDATES

Ag_2SO_4, H_2SO_4 on Gas-Chrom P
$HgSO_4$, H_2SO_4 on GC-22
$Hg(ClO_4)_2$, $HClO_4$ on Gas-Chrom P
40% $Hg(ClO_4)_2$ on GC-22
10% 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) on Anakrom ABS
DDQ, di(2-ethylhexyl)sebacate on Anakrom ABS
5A Molecular Sieve
10% $Cr_2(SO_4)_3$ on Porasil C
10% Na_2SO_4 on Porasil C
20% NaBr on F-20 alumina
20% NaOH on F-20 alumina
H_3BO_3, Carbowax 20M on Chromosorb P
B_2O_3, Carbowax 20M on GC-22
5% H_3BO_3 on GC-22
$LiBH_4$ powder
$LiAlH_4$ powder
10% $LiAlH_4$ on GC-22

also abstracted but all other classes tested passed through the column quantitatively at 30°. In an effort to minimize retention volumes for those classes not abstracted, the column was heated to 125°. Apparent dehydration occurred which seriously degraded the column's performance. Therefore, this abstractor candidate can be used as a heavy ends unsaturate and oxycarbon abstractor.

Another unsaturate abstractor, $Hg(ClO_4)_2$, $HClO_4$ on Gas-Chrom P[2-4], did not quantitatively abstract ethene, propene, and propyne at 100°. The higher unsaturates, as well as most oxycarbons, were quantitatively abstracted. However, some loss of aromatics occurred as well. The mixed behavior of this substrate makes it a poor candidate for use in the Class Analyzer.

Coating GC-22 with 40% $Hg(ClO_4)_2$[5] produced a substrate which quantitatively abstracted all unsaturates, aromatics, and oxycarbons tested. The saturates were only slightly retained at 125°. Some loss of halocarbons occurred, however. With the exception of halocarbons, this substrate behaved well enough to be used as a light ends unsaturate abstractor and a heavy ends abstractor for unsaturates, aromatics, and oxycarbons.

The charge transfer complex formed between lower aromatics and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was too weak to cause abstraction of aromatics. The behavior was similar when DDQ was either coated directly on Anakrom ABS or dissolved in di(2-ethylhexyl) sebacate before coating. DDQ is temperature sensitive, so both columns were tested at 30° initially. When no aromatic abstraction occurred, the temperature was raised to 75° for the liquid solution coating and 225° for the solid coating. The only change was partial decomposition of DDQ. Neither column abstracted any hydrocarbon class, so no further evaluation was performed.

Molecular Sieves have been used for selective hydrocarbon separations by several investigators.[7,8] However, our experience with 5A Molecular Sieve was that quantitative separations were extremely

difficult over a temperature range from 30° to 200°. Almost every hydrocarbon tested was partially abstracted. Such performance does not meet the criteria of an ideal class abstractor.

Salt-coated silica and alumina have shown promise as being selective hydrocarbon class abstractors.[9,10] Four columns were made: 10% $Cr_2(SO_4)_3$ on Porasil C, 10% Na_2SO_4 on Porasil C, 20% NaBr on F-20 alumina, and 20% NaOH on F-20 alumina. In terms of their performance as class abstractors, all columns performed similarly. Oxycarbons were abstracted but all other classes were strongly retained, even at 200°. This strong retention greatly increases the time required for analysis. Attempts to deactivate Porasil C and alumina with water injected into the columns had no beneficial effect. The conclusion is that these adsorbents are much too active for use in the Class Analyzer and no suitable deactivation procedure could be found.

Boric acid reacts with most alcohols to form non-volatile borate esters. This reaction has been utilized in designing alcohol abstractors.[11,12] A substrate of 3% boric acid and 20% Carbowax 20M on Chromosorb P merely retained alcohols at 175°. This retention was strong enough to permit a separation of alcohols from other hydrocarbon classes tested, but such performance is clearly inferior to total abstraction.

Because partially dehydrated boric acid is thought to be the reactant, a 3% boric anhydride and 20% Carbowax 20M substrate was prepared. However, all classes tested passed through the column with no abstraction and very weak retention occurring. Obviously, totally dehydrated boric acid (boric anhydride) is unreactive toward alcohols.

Preconditioning a 5% boric acid on GC-[illegible] column at 300° permitted substantial, but not complete dehydration to occur. The resulting column abstracted primary and secondary alcohols quantitatively at 125°. Tertiary alcohols appeared to be dehydrated to alkenes rather than being abstracted. All other classes pass through the

column quite rapidly with no apparent losses. This column was not incorporated into the Class Analyzer only because a better column was subsequently found.

The reducing agents, $LiBH_4$ and $LiAlH_4$, react with oxycarbons to form non-volatile complexes. $LiBH_4$ is more thermally stable than $LiAlH_4$, but is more hygroscopic and difficult to handle. Its performance as an oxycarbon abstractor is inferior also. At temperatures from 100° to 200°, $LiBH_4$ abstracts only higher oxycarbons such as cyclohexanone, 4-methylbutanol, and 2-ethylhexanol. Lower oxycarbons are not abstracted at all.

$LiAlH_4$ is reported to decompose from 130° to 187°, depending on the source of information. At 130°, $LiAlH_4$ abstracts all oxycarbons tested initially, but after about 40 hours of operation at 130°, acetone and ethyl acetate are not quantitatively abstracted. This may be due to decomposition. However, operation at 120° results in no appreciable acetone abstraction, so the operating temperature must be kept near 130° for ideal performance. All other classes are unaffected by $LiAlH_4$.

A problem with using $LiAlH_4$ powder as a substrate is its high back pressure and propensity for clogging. Coating a chromatographic support with $LiAlH_4$ was attempted by dissolving it in diethyl ether. However, the moisture present in the solvent and the atmosphere rapidly diactivates $LiAlH_4$ and forms an insoluble precipitate. A source of 1.3M $LiAlH_4$ in diethyl ether was found. This made coating GC-22 with a 10% layer of $LiAlH_4$ possible. This procedure produces a substrate which does not cause any gas flow problems.

An additional problem with $LiAlH_4$ is its reactivity with moisture in the sample. Not only does the moisture deactivate $LiAlH_4$, but the reaction appears to release previously abstracted oxycarbons. This problem was discovered only after a $LiAlH_4$ column had been installed in the Class Analyzer. A solution to the problem would be the installation of a desiccant in the stack sampler and/or immediately upstream of the $LiAlH_4$ column. Further research is necessary to optimize this system.

CLASS ANALYZER

The final configuration of the Class Analyzer is shown in Figure 7. The selection of abstractor columns was based on their performance during the evaluation phase.

Testing of the Class Analyzer was conducted by making syringe injections of model compounds into the Class Analyzer. This was made possible by connecting the UC by-pass (with its septum) to the Class Analyzer.

Testing revealed several problems. Initially, sample losses exceeded 50%. The cause of these excessive losses was a series of small but troublesome leaks in the swaged tubing connections. Correction of these leaks eliminated all but roughly 10% of the losses. These losses can only be attributed to wall losses within the system itself. By enclosing as much of the system as possible in a heated compartment, these losses should be minimized.

Tests involving cryogenic trapping revealed a background level of hydrocarbons in the system which would prohibit the detection of hydrocarbons in a sample below about 0.1 ppm. The source of this background is probably those hydrocarbons which are slowly being released from the walls of the system tubing. Carrier gas contamination was minimized by passing 99.996% helium through a Molecular Sieve and charcoal trap at -196°. Another source of background hydrocarbons is from the $LiAlH_4$ column. Moisture in the sample can release previously abstracted oxycarbons.

The loss of trapped methane was a concern. Devarda's metal in the cryogenic trap minimizes this loss.[13] Because of methane's substantial vapor pressure even as a solid at -196°, the amount of methane lost depends on the volume of carrier gas which flows through the trap. Our tests indicate that very little methane is lost during the trapping phase, when 300 ml of carrier are passed through the trap. Methane is apparently displaced along the length of the trap as carrier gas flows through the trap. As long as the trap is sufficiently long, little methane should be lost. Quantitative studies have not been performed.

TOTAL SYSTEM TESTING

Testing of the entire sampling-analysis system was attempted. Ideally, actual samples from a variety of industrial operations were to be collected.

Field testing locations were sought at the beginning of the program. The Project Officer suggested that early arrangements be made to avoid later complications. A list of over 75 potential field test sites was compiled from suggestions made by the Los Angeles Air Pollution Control District, from ARLI clients, and from companies listed in the Telephone Directory. These test sites included chemical manufacturing plants, paint and varnish works, degreasers, solvent reclaimers, printing operations, petroleum refineries, and power plants.

The most serious difficulty in finding suitable test sites was the problem of using the Method 5 stack sampler for sampling. The Method 5 equipment is quite heavy and bulky. Substantial support must be provided to make sampling physically possible and to protect the delicate glassware in the sampling unit. The support rail of the Joy Method 5 sampler attaches to a clamp which fits over a standard 7.6 cm (3 in.) test port. In all the many contacts made with representatives of potential test sites, a stack equipped with a standard test port was never found.

The second problem was the lack of cooperation of many company executives. Those at the larger plants having high capacity stacks suitable for sampling were not agreeable to having EPA contractors sampling their emissions.

Some potential test sites did not emit hydrocarbons that were suitable for our sampling needs. Frequently, the emissions contained only one or two components, rather than the variety that was sought.

In several instances, sampling access was arranged only to be postponed indefinitely or cancelled due to alleged breakdowns, changes in the company's attitude toward the agreed-upon arrangements etc.

In order to test the sampler, small companies whose emissions emanated from small roof vents, had to be relied upon. An unheated Pyrex glass sample probe was fabricated to replace the long stack sampler pitobe for this type of sampling.

When the difficulties of finding suitable test sites became critical, a laboratory test stack was constructed. The test stack permitted the operation of the Method 5 sampler in its intended mode. Also, a variety of different types of samples could be prepared for testing. Unfortunately, use of this simulator was not initiated until late in the program, so that only a limited number of tests could be undertaken.

Our first test mixture (EPA-1) consisted of an equimolar mixture of hexane, 1-hexene, benzene, and methanol. This liquid mixture was infused into the test stack at the rate of about 0.38 ml/min. The test stack air flow was about 6700 l/min. This provided a stack sample containing approximately 14 ppm total hydrocarbons in addition to the comparatively minor contribution from the ambient air.

During the actual test sampling, the stack gas temperature and relative humidity were $24.5 \pm 0.5^{\circ}$ and $50 \pm 5\%$, respectively. The pitobe and filter oven were maintained at $125 \pm 10^{\circ}$. The Universal Collector and the Method 5 impingers were kept at 0°. The total sampling rate through the Method 5 train was 28 l/min with 55 ml/min passing through the Universal Collector. Each Universal Collector was in operation for 7 min 16 sec resulting in a sample volume of 400 ml. The pitobe inlet was positioned at the center of the stack for all six Universal Collectors.

Prior to installing the first Universal Collector, the stack blower, the syringe infusion pump, and the Method 5 sampler pump were activated to permit a stable equilibrium condition to be established. As the first Universal Collector was installed, a grab sample was collected in an evacuated stainless steel bomb as closed to the pitobe inlet as possible.

Gas chromatographic analysis of the grab samples indicated that the sample composition was not uniform during the sampling period. Probable causes were non-uniformities in the sample volatilization and dispersion in the stack gas stream.

The results of the analysis of sample EPA-1 are tabulated in Table 5. The data for two of the collectors are not shown. The contents of UC 6 were lost because of problems in operating the Class Analyzer. Pressure surges during valve actuation caused FID extinguishment. Plumbing modifications alleviated this problem. UC 2 apparently leaked during the storage period between sampling and analysis. The automatic shut-off, quick-disconnect fittings can leak if the end of the fitting is placed against a flat surface.

Operator error caused FID extinguishment during the analysis of UC 5. The entire sample was not lost, however, and those data that were obtained are shown.

The method of calculation is as follows:

$$C_S = (P'_{L-2} + P'_{H-2})R_S/V$$

$$C_U = (P'_{L-1} - P'_{L-2} + P'_{H-3} - P'_{H-4})R_U/V$$

$$C_A = (P'_{H-4} - P'_{H-2})R_A/V$$

$$C_O = (P'_{H-1} - P'_{H-3})R_O/V$$

$$P'_i = P_i(F_{ave}/F_i)$$

where C = concentration of a specific hydrocarbon class, mg/m^3

P = raw peak area, cm^2

P' = corrected peak area, cm^2

R = detector response factor, 10^6 mg/cm^2

V = sample volume, ml

F = flow rate, ml/min

S = saturate class

U = unsaturate class

A = aromatic class

Table 5. CLASS ANALYZER ANALYSIS OF SAMPLE EPA-1

	Concentration of component, mg/m^3				
UC	Hexane	1-Hexene	Benzene	Methanol	Total
1	3.75	6.43	0.46	10.20	20.84
3	3.67	6.32	3.98	-0.23	13.74
4	3.74	9.33	2.47	-0.90	14.64
5	3.22	-	5.11	-	-

O = oxycarbon class
L = light end stream
H = heavy end stream

The precision of the saturate analysis (represented by hexane) was reasonably good. This is partly due to the mode of sample concentration calculation. When no light end components are present, the saturate calculation is the only calculation which does not require two peak area determinations and the inherent increase in error. The saturate determination is calculated directly from the effluent of stream H-2.

The aromatic and oxycarbon data are clearly not satisfactory. This is probably due to moisture in the sample which causes the $LiAlH_4$ column to elute oxycarbons which had been abstracted earlier. The same $LiAlH_4$ column is in both streams H-3 and H-4, thus causing erratic results in both the aromatic and oxycarbon determinations. The unsaturate determination is fairly good. Here the difference in effluent from H-3 and H-4 is involved in the unsaturate determination, so that the above-mentioned error cancels.

Modifications were made to the stack sampler, the Class Analyzer, and the sampling and analytical procedures as a result of the experience with sample EPA-1. After these modifications had been completed, sample EPA-2, a 24-hour ambient air sample, was collected.

The 24-hour ambient air sample was collected continuously on 7 and 8 November 1974. The lowest flow rate attainable through the hydrocarbon sample train at present is 2 ml/min. Using the sample size limitation of 400 ml, only 3 hr 20 min of continuous sampling is possible. With only 6 UC's available and about 10 minutes allowed for a change of UC's, only 21 hours of sampling could be accomplished. The decision was made to increase the sample size limit to permit a full 24 hour sampling period at the possible risk of losing a small amount of methane.

Each UC collected about 454 ml of sample over a 3 hour 47 minute period. Allowing about 13 minutes for a change of UC's, the total sampling period was 24 hours. The meteorological conditions varied from 6°C and 86% relative humidity to 26°C and 32% relative humidity. The air was clear and still during the entire sampling period. The Los Angeles Air Pollution Control District reported maxima of 0.08 - 0.09 ppm O_3, 13-15 ppm CO, and 0.12 - 0.36 ppm NO_x during the sampling period.

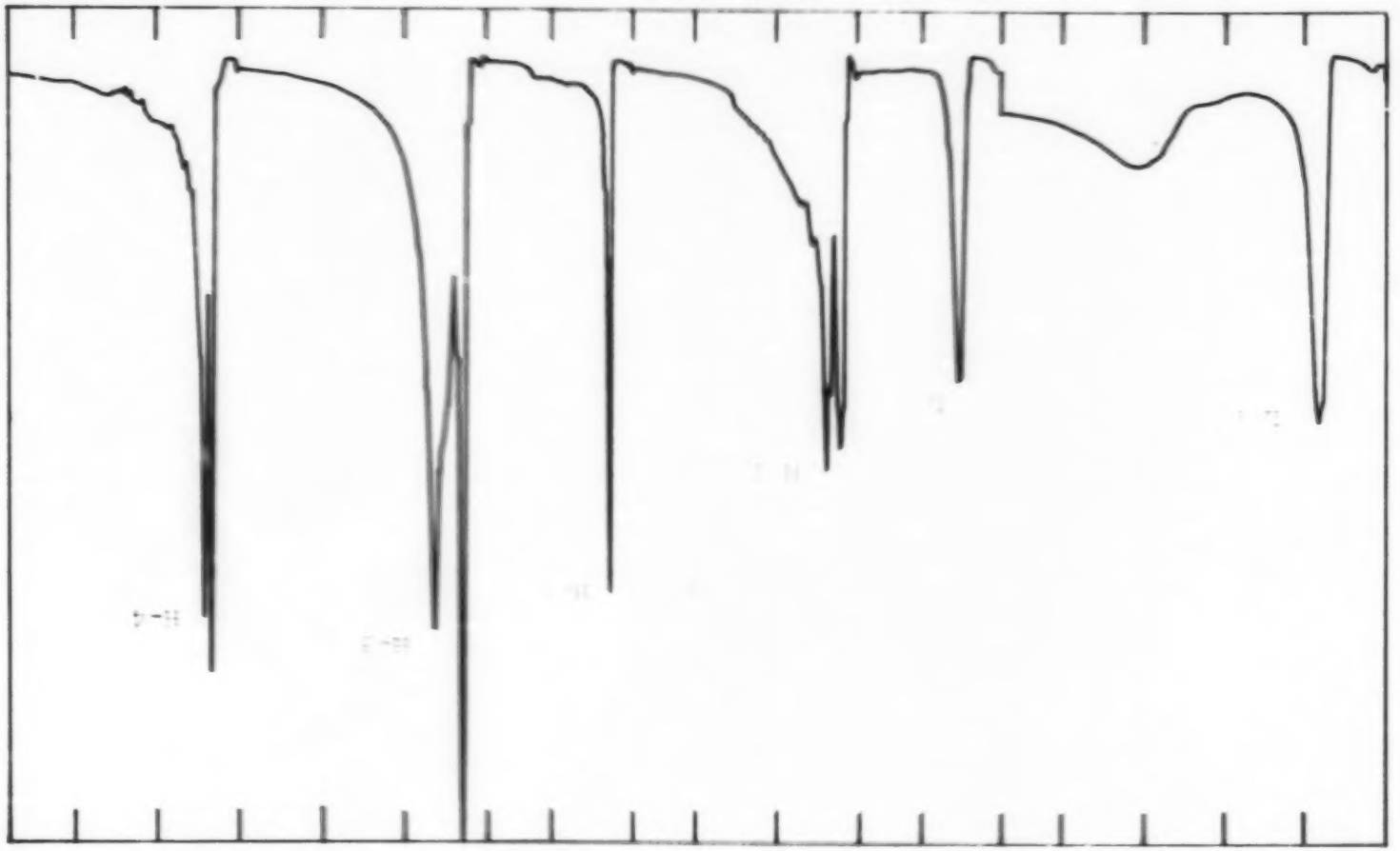
The results of the analysis are tabulated in Table 6. An integration error prevented the determination of the FID response which is used to calculate the light end unsaturate concentration in UC 1. Otherwise, the analysis went smoothly. The saturate levels followed a pattern that parallels the level of automobile traffic in the Los Angeles Basin. The saturate levels are at a minimum during the late night and early morning hours (UC's 4 and 5) and at a maximum during daylight hours (UC's 1, 2, and 6). The light unsaturates and the aromatic levels appear to be reasonable. The oxycarbon and heavy unsaturate levels reflect too much effluent from stream H-3. Again, water vapor in the air sample is probably responsible for this difficulty.

Typical examples of the output signal from the Class Analyzer are shown in Figure 13. The ideal, sharp, Gaussian peak shape does not occur in all cases. The multiple or broadened peaks are doubtless due to fractionation of the sample as it is being vaporized from the cryogenic traps. More rapid vaporization would probably improve the peak shape and thus simplify the concentration determination.

One additional problem was accentuated during this analysis: excessive sample contamination by the AC charcoal bed in the UC. This can be seen as the broad peak in the chromatogram of stream L-1 in Figure 13. The next sample to be analyzed was a synthetic light hydrocarbon sample. However, the analysis was postponed

Table 6. CLASS ANALYZER ANALYSIS OF SAMPLE EPA-?

UC	Sampling period, PST	Component concentrations, mg/m^3					
		Saturates		Unsaturates			
		Light	Heavy	Light	Heavy	Aromatics	Oxycarbons
1	10-14	0.99	0.30	-	-0.14	0.56	0.46
2	14-18	0.81	0.55	0.57	0.57	0.49	-0.33
3	18-22	0.25	0.31	0.08	0.14	0.54	-3.04
4	22-02	0.74	0.10	0.12	0.43	0.56	-0.60
5	02-06	0.21	0.08	0.47	0.13	0.21	-0.09
6	06-10	0.80	0.13	0.68	0.13	0.15	0.41



until the charcoal contamination could be investigated.

Conditioning of AC charcoal at 200° under helium flow does not sufficiently clean the charcoal surface of adsorbed hydrocarbons. Conditioning at 300° in vacuo overnight reduces but does not eliminate the contamination. Conditioning at 550° in vacuo eliminates the contamination but results in such an active charcoal surface that C-2 and C-3 hydrocarbons exhibit some irreversibility of adsorption (i.e., sample loss occurs). The ideal conditioning procedure has not been found as yet.

In addition to the light hydrocarbon sample, two additional samples were to be collected and analyzed. These were the effluents from: (1) a paint spray booth; and (2) from a printing operation. However, scheduling and budgetary constraints forced the cancellation of these tests.

The sampling and analytical hardware were being improved with each sample that was collected. Presently, a sample can be broken down into saturate and non-saturate fractions with good reliability. This in itself is a valuable analysis because saturates are generally quite innocuous as pollutants while non-saturates tend to be more photo-reactive and noxious.

Samples were stored for 30 days in several UC's in a storage freezer (-5°C) with no apparent changes in the samples noted. The retention characteristics of the UC's themselves did not appear to change over the course of the research effort. If the UC is not overheated, physically damaged, or irreversibly contaminated, life of usage should be indefinite.

With additional development effort and equipment redesign, the determination of hydrocarbon class content in stationary source emissions can become a routine analytical procedure.

SECTION VII

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